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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 show an upward flux with a maximum early in the morning, and the measured fluxes are in agreement with what is expected from the positive 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

The Amazonia rainforest has been subject to continued deforestation and land-use expansion that is typical of tropical forests worldwide. Common land-use practices in the Brazilian Amazon include cattle ranching, logging, agriculture, mining, and urbanization. Since tropical rainforests play a prominent role in the global carbon and methane cycle, land use change implies numerous modifications to the biogeochemical cycles. Numerous studies have been carried out to understand the role of the tropical forest in

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the global cycle of the main greenhouse gases (Andreae et al., 2002; de Araújo et al., 2002; Bergamaschi et al., 2009; 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, 1983; Sanhueza and Donoso, 2006).

Methane (CH_4) is the second most important anthropogenic greenhouse gas and its mixing ratio (presently ~ 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 per kg 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., 2009; Dlugokencky et al., 1998), isotope measurements (Quay et al., 1999; Miller et al., 2002), forward and inverse modeling (Bousquet et al., 2006; Meirink et al., 2008; Bergamaschi et al., 2009) and recently also satellite remote sensing (Frankenberg et al., 2005, 2008). It is now well-established that CH_4 is emitted from various biogenic, anthropogenic and geological sources, (IPCC, 2007; Etiope and Klusman, 2002). The main way to remove methane from the troposphere is through oxidation by OH radicals. Microbial oxidation in aerobic soils, and transport to the stratosphere are minor sinks for atmospheric CH_4 (IPCC, 2001).

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

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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).

Keppler et al. (2006) reported aerobic methane emissions from dead and living biomass in laboratory incubation experiments, but these results have been heavily debated. For dry biomass, plant litter and plant structural components, emissions of methane and other reduced hydrocarbons under the influence of UV light and temperature have been confirmed (McLeod et al., 2008; Vigano et al., 2008, 2009, 2010; Keppler et al., 2008; Messenger et al., 2009; Bruhn et al., 2009). For living plants, however, the original extrapolations appear to be at least a strong overestimate, as initially noted by (Houweling et al., 2006; Ferretti et al., 2007; Butenhoff and Khalil, 2007; Kirschbaum et al., 2006; Kirschbaum et al., 2007). However, only few additional experiments were carried out. Dueck et al. (2007) and Beerling et al. (2008) found no evidence for emissions from living plants, Bruggemann et al. (2009) found emissions, but of much smaller magnitude. Significant CH_4 emissions were reported in several other studies (Wang et al., 2009; Wang et al., 2008; Kitaoka et al., 2007; Qaderi and Reid, 2009; Cao et al., 2008). 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.

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 $Tg\,y^{-1}$, 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

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methane emissions from the Amazon basin. They calculate emissions averaging 20 mg CH_4 m^{-2} day^{-1} from the area around Manaus.

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), 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).

Currently, long term methane flux measurements are mostly performed using closed gas chamber techniques (e.g., Kiese et al., 2003; Singh et al., 1997; Verchot et al., 2000). Closed chambers are relatively simple in operation and inexpensive. On the other hand, such measurements are not continuous and the technique itself is prone to a variety of potential errors (Kutzbach et al., 2007). Direct flux measurements use the Eddy Covariance technique (EC) and do not affect the natural gas transfer process while giving flux estimates on the ecosystem level and for a more representative area (Smeets et al., 2009; Hendriks et al., 2008; Vesala et al., 2008). Typical footprint areas are tens of m^2 to several ha of the surface area upwind from the tower (Kljun et al., 2002). EC is suitable to determine surface fluxes successfully during daytime or weakly stable conditions, but it is more problematic when turbulence is too small or intermittent (Pattey et al., 2002).

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.

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2 Methodology

2.1 Site description

The Amazonia rainforest is well known for its diverse fauna and flora and peculiar characteristics in topography. Around 50% of Amazonia is terra firme forest. This type of forest is characterized by dense closed canopy and detains a rich diversity of tree species (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 is formed by plateaus and valleys (around 60%) with maximum height differences of about 60 m. This 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, and the valley soil is usually waterlogged during the rainy season (Chambers et al., 2004; Luizão et al., 2004). 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).

2.2 Flux measurements

The EC instruments were installed on a 53 m tall scaffolding flux tower called K34 (Fig. 1), which was erected in 1999. It is a $1.5 \times 2.5\,m^2$ 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). 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

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a memory card. The FMA was operated in a closed-path 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 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). Most importantly, the closed path data from the FMA had to be combined with open path H_2O data, which requires corrections. 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 m^{-1} over a period of 6 h by a metal bellows pump model MB-118E, and collected in 2 L 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. To avoid air contamination, 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

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(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).

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 1 L 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^{TM} with moisture indicator, which was replaced when it was 75% purple. After sampling, the glass flasks were stored in an aluminum box and sent for analysis to LQA/IPEN.

2.4 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 obteined 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.

3 Results

3.1 Rainfall and soil moisture

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,

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rainfall is present throughout the year, but 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 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 at 0.3, 0.5 and 1 m respectively.

3.2 Calibration of the online measurements by flask samples

During May and June 2009, weekly flask samples were taken at the top of the K34 tower, where the FMA operates. 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 was calculated. We corrected the FMA data assuming that this offset was constant throughout the campaign.

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3.3 Vertical gradients

An intensive campaign to measure vertical CH_4 mixing ratio gradients in the canopy was carried out in November–December 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.) 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 result is shown in Fig. 5c and d with the average differences printed in red. During daytime, 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.

3.4 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 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,

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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 flux data.

3.5 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. Tota 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

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is clear that in order to further examine this feature for CH_4, high temporal resolution measurements are required, which requires in-situ measurements. 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 (December 2008–January 2009). 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 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 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.

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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.

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 ~ 9 µmol m^{-2} s^{-1} for CO_2 between 07:00 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 (Tota 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 6 h. After ~ 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 (~ 06 : 00 p.m. local time), as was observed by (de Araújo et al., 2002; 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 at calm nights is limited due to the absence of turbulence. Also surface cooling at night suppresses vertical transport and increases horizontal advection possibly leading to an underestimate of emissions during calm

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and clear nights (Goulden et al., 2006). However, for CH_4, the nighttime fluxes are identical to the fluxes measured during the afternoon, where conditions for flux measurements are 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 a different Amazon rainforest station in Rondonia (Simon et al., 2005) showed canopy flushing rates of ~ 1 h at 90% canopy height. We note that the canopy at the 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 for a rough estimate. From the gradient results in Fig. 5, we estimate that a CH_4 excess of ~ 5 ppb $\times$ 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 rough estimate is of similar magnitude as the nighttime fluxes ~ 1 nmol m^{-2} s^{-1} that we measured in November, and thus it provides independent support that the nighttime methane fluxes are positive and have the correct magnitude. Under the assumptions stated above, the positive gradients within the canopy are in rough quantitative agreement with the fluxes detected above the canopy, i.e., the 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 ~ 2 nmol m^{-2} s^{-1}, which corresponds to ~ 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 aircraft flights in the Manaus Amazon basin. It follows that the measured emissions from the upland forest reported here can account for ~ 14% of the total flux, which is certainly dominated by wetland emissions. Also from the total averaged measured flux we estimate the annual CH_4 production. Multiplying ~ 2.8 mg CH_4 m^{-2} day^{-1} by the total upland forest area in

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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).

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. It is evident that the effect of decreasing CH_4 mixing ratios from the breakup of the boundary layer is much stronger than the flux from the canopy venting peak as discussed above, since the positive flux from the canopy should actually lead to an increase of CH_4 above the canopy. But this peak comes at a time when the nighttime boundary layer is already dissolving so the flux from below does not lead to a significant increase of CH_4 above canopy.

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_4mixing 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^{-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 µmol m^{-2} h^{-1}, or 2 nmol m^{-2} s^{-1}.

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This is of the order of the observed mean nighttime flux between 0.5 and 4 nmol 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 about 05 h. 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 organic decomposition at the soil is the most important source for the CH_4 budget at this site.

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Appendix A

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

Scalars and water vapor appear to 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 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 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

$$H(f) = \frac{1}{1+(f/f_c)^2} \tag{A1}$$

where f_c is the cut-off frequency (the frequency at which the filter reduces the power spectral estimates by a factor 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 meteorological tower in Cabauw (The Netherlands) 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 analyser. 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 and displayed in Fig. 8 together with the empirical model from Ibrom et al. (2007).

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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 1).

Appendix B

The validity of the nighttime CH_4 fluxes

For a correct estimate of the closed path measured methane fluxes we estimated its maximum value via a trial and error method that repeatedly calculates covariance for a range of lag times between w' and CH_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).

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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. 9 we display the averaged diurnal variation of methane fluxes and the corresponding detection limit for the whole measurement period. In particular in the second half of the night (after midnight), the measured fluxes are above the detection limit. Before midnight, they are of the same order or slightly below the detection limit, but note that the detection limit is calculated for one single half-hour period, and our data are averages over many days. 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 h and 05 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. 10. 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 proof for the high quality of our EC measurements. The shape and noise of the co-spectrum of CH_4 compares very well to the other co-spectra, which confirms the good quality of the CH_4 measurement by the FMA and the validity of upward directed nighttime methane fluxes. The increase of the co-spectral values for methane fluxes above $f = 0.3$ Hz is due to the influence of relatively high signal noise present in the methane mixing ratio

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measurements. This issue including the correction of the fluxes for this part of the co-spectrum was described by Smeets et al. (2009).

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References

Andreae, M. O., Artaxo, P., Brandão, C., Carswell, F. E., Ciccioli, P., da Costa, A. L., Culf, A. D., Esteves, J. L., Gash, J. H. C., Grace, J., Kabat, P., Lelieveld, J., Malhi, Y., Manzi, A. O., Meixner, F. X., Nobre, A. D., Nobre, C., Ruivo, Md. L. P., Silva-Dias, M. A., Stefani, P., Valentini, R., von Jouanne, J., and Waterloo, M. J.: Biogeochemical cycling of carbon, water, energy, trace gases and aerosols in Amazonia: The LBA-EUSTACH experiments, J. Geophys. Res., 107, 8066, doi:10.1029/2001JD000524, 2002.

Bartlett, K. B. and Harriss, R. C.: Review and assessment of methane emissions from wetlands, Chemosphere, 26, 261–320, 1993.

Beerling, D. J., Gradiner, T., Leggett, G., McLeod, A., and Quick, W. P.: Missing methane emissions from leaves of terrestrial plants, Glob. Change Biol., 14, 1–6, doi:10.1111/j.1365-2486.2008.01607.x, 2008.

Bergamaschi, P., Frankenberg, C., Meirink, J. F., Krol, M., Villani, M. G., Houweling, S., Dentener, F., Dlugokencky, E. J., Miller, J. B., Gatti, L. V., Engel, A., and Levin, I.: Inverse modeling of global and regional CH_4 emissions using SCIAMACHY satellite retrievals, J. Geophys. Res., 114, D22301, doi:10.1029/2009JD012287, 2009.

Bousquet, P., Ciais, P., Miller, J. B., Dlugokencky, E. J., Hauglustaine, D. A., Prigent, C., Van der Werf, G. R., Peylin, P., Brunke, E. G., Carouge, C., Langenfelds, R. L., Lathiere, J., Papa, F., Ramonet, M., Schmidt, M., Steele, L. P., Tyler, S. C., and White, J.: Contribution of anthropogenic and natural sources to atmospheric methane variability, Nature, 443, 439–443, 2006.

Bruggemann, N., Meier, R., Steigner, D., Zimmer, I., Louis, S., and Schnitzler, J. P.: Nonmicrobial aerobic methane emission from poplar shoot cultures under low-light conditions, New Phytol., 182, 912–918, 2009.

ACPD
11, 5313–5350, 2011

Bruhn, D., Mikkelsen, T. N., Obro, J., Willats, W. G. T., and Ambus, P.: Effects of temperature, ultraviolet radiation and pectin methyl esterase on aerobic methane release from plant material, Plant. Biology, 11, 43–48, 2009.

Butenhoff, C. L. and Khalil, M. A. K.: Global methane emissions from terrestrial plants, Environ. Sci. Technol., 41, 4032–4037, 2007.

Cao, G. M., Xu, X. L., Long, R. J., Wang, Q. L., Wang, C. T., Du, Y. G., and Zhao, X. Q.: Methane emissions by alpine plant communities in the Qinghai-Tibet Plateau, Biol. Letters, 4, 681–684, 2008.

Carmo, J. B., Keller, M, Dias, J. D., Camargo, P. B., and Crill, P.: A source of methane from upland forests in the Brazilian Amazon, Geophys. Res. Lett., 33, L04809, doi:10.1029/2005GL025436, 2006.

Chambers, J. Q., Tribuzy, E. S., Toledo, L. C., Crispim, B. F., Higuchi, N., Santos, J. dos, de Araújo, A. C., Kruijt, B., Nobre, A. D., and Trumbore, S.: Respiration from a tropical forest ecosystem: partitioning of sources and low carbon use efficiency, Ecol. Appl., 14(4), S72–S88, Supplement, 2004.

Culf, A. D., Fisch, G., Malhi, Y., and Nobre, C. A.: The influence of the atmospheric boundary layer on carbon dioxide concentrations over a tropical forest, Agr. Forest Meteorol., 85, 149–158, 1997.

Crutzen, P. J., Sanhueza, E., and Brenninkmeijer, C. A. M.: Methane production from mixed tropical savanna and forest vegetation in Venezuela, Atmos. Chem. Phys. Discuss., 6, 3093–3097, doi:10.5194/acpd-6-3093-2006, 2006.

de Araújo, A. C.: Spatial variation of CO_2 fluxes and lateral transport in an area of terra firme forest in central Amazonia, PhD Thesis, Vrij University of Amsterdam, 2009.

de Araújo, A. C., Nobre, A. D., Kruijt, B., Elbers, J. A., Dallarosa, R., Stefani, P., von Randow, C., Manzi, A. O., Culf, A. D., Gash, J. H. C., Valentini, R., and Kabat, P.: Comparative measurements of carbon dioxide fluxes from two nearby towers in a central Amazonian rainforest: The Manaus LBA site, J. Geophys. Res., 107, 8090, doi:10.1029/2001JD000676, 2002.

de Araújo, A. C., Kruijt, B., Nobre, A. D., Dolman, A. J., Waterloo, M. J., Moors, E. J., and Souza, J. S.: Nocturnal accumulation of CO_2 underneath a tropical forest canopy along a topographical gradient, Ecologica Application, 18(6), 1406–1419, 2008a.

de Araújo, A. C., Nobre, A. D., Kruijt, B., Culf, A.D., Stefani, P., Elbers, J., Dallarosa, R., von Randow, C., Manzi, A. O., Valentini, R., Gash, J. H. C, Kabat, P.: Dual tower long-term study of carbon dioxide fluxes for a central Amazonian rain forest: The Manaus LBA site, J.

ACPD
11, 5313–5350, 2011

Geophys. Res, 107(D20), 8090, doi:10.1029/2001JD000676, 2009.
de Araújo, A. C., Dolman, A. J., Waterloo, M. J., Gash, J. H. C., Kruijt, B., Zanchi, F. B., de Lange, J. M. E., Stoevelaar, R., Manzi, A. O., Nobre, A. D., Lootens, R. N., and Backer, J.: The spatial variability of CO_2 storage and the interpretation of eddy covariance fluxes in central Amazonia, Agr. Forest Meteorol., 150, 226–237, 2010.
Dlugokencky, E. J., Masarie, K. A., Lang, P. M., and Tans, P. P.: Continuing decline in the growth rate of the atmospheric methane burden, Nature, 393, 447–450, 1998.
Dlugokencky, E. J., Myers, R. C., Lang, P. M., Masarie, K. A., Crotwell, A. M., Thoning, K. W., Hall, B. D., Elkins, J. W., and Steele, L. P.: Conversion of NOAA atmospheric dry air CH_4 mole fractions to a gravimetrically prepared standard scale, J. Geophys. Res., 110, D18306, doi:10.1029/2005JD006035, 2005.
Dlugokencky, E. J., Bruhwiler, L., White, J. W. C., Emmons, L. K., Novelli, P. C., Montzka, S. A., Masarie, K. A., Lang, P. M., Crotwell, A. M., Miller, J. B., and Gatti, L. V.: Observational constraints on recent increases in the atmospheric CH_4 burden, Geophys. Res. Lett., 36, L18803, doi:18810.11029/12009gl039780, 2009.
Dueck, T. A., de Visser, R., Poorter, H., Persijn, S., Gorissen, A., de Visser, W., Schapendonk, A., Verhagen, J., Snel, J., Harren, F. J. M., Ngai, A. K. Y., Verstappen, F., Bouwmeester, H., Voesenek, L. A. C. J., and van der Werf, A.: No evidence for substantial aerobic methane emission by terrestrial plants: a ^{13}C-labelling approach, New Phytol., 175, 29–35, doi:10.1111/j.1469-8137.2007.02103.x, 2007.
Etheridge, D. M., Steele, L. P., Francey, R. J., and Langenfields, R. L.: Atmospheric methane between 1000 A.D. and present: Evidence of anthropogenic emissions and climatic variability, J. Geophys. Res., 103, 15979–15993, 1998.
Etiope, G. and Klusman, R. W.: Geologic emissions of methane to the atmosphere, Rev. Chemosphere, 49, 777–789, 2002.
Ferretti, D. F., Miller, J. B., White, J. W. C., Lassey, K. R., Lowe, D. C., and Etheridge, D. M.: Stable isotopes provide revised global limits of aerobic methane emissions from plants, Atmos. Chem. Phys., 7, 237–241, doi:10.5194/acp-7-237-2007, 2007.
Frankenberg, C., Meirink, J. F., van Weele, M., Platt, U., and Wagner, T.: Assessing methane emissions from global space-borne observations, Science, 308(5724), 1010–1014, doi:10.1126/science.1106644, 2005.
Frankenberg, C., Bergamaschi, P., Butz, A., Houweling, S., Meirink, J. F., Notholt, J., Petersen, A. K., Schrijver, H., Warneke, T., and Alben, I.: Tropical methane emissions:

ACPD
11, 5313–5350, 2011

A revised view from SCIAMACHY onboard ENVISAT, Geophys. Res. Lett., 35, L15811, doi:10.1029/2008GL034300, 2008.
Goulden, M. L., Miller, S. D., and da Rocha, H. R.: Nocturnal cold air drainage and pooling in a tropical forest, J. Geophys. Res., 11, D08S04, doi:10.1029/2005JD006037, 2006.
Hendriks, D. M. D., Dolman, A. J., van der Molen, M. K., and van Huissteden, J.: A compact and stable eddy covariance set-up for methane measurements using off-axis integrated cavity output spectroscopy, Atmos. Chem. Phys., 8, 431–443, doi:10.5194/acp-8-431-2008, 2008.
Houweling, S., Röckmann, T., Aben, I., Keppler, F., Krol, M., Meirink, J. F., Dlugokencky, E., and Frankenberg, C.: Atmospheric constraints on global emissions of methane from plants, Geophys. Res. Lett., 33, L15821, doi:15810.11029/12006GL02616, 2006.
IPCC: Contribution of Working Group 1 to the Third Assessment Report of the Intergovernmental Panel on Climate Change, in: Climate Change, The Scientific Bases, edited by: Houghton, J. T., Ding, Y., Griggs, D. J., Nouguer, M., van der Linden, P. J., Dai, X., Maskell, K., Johnson, C. A., Cambridge University Press, Cambridge, UK, 10–64, 2001.
IPCC: Fourth Assessment Report, Climate Change, Cambridge University Press, Cambridge, 2007.
Itoh, M., Ohte, N., and Koba, K.: Methane flux characteristics in forest soils under an East Asian monsoon climate, Soil Biol. Biochem., 41(2), 388–395, 2009.
Ibrom, A., Dellwik, E., Flyvbjerg, H., Jensen, N. O., and Pilegaard, K.: Strong low-pass filtering effects on water vapour flux measurements with closed-path eddy correlation systems, Agr. Forest Meteorol., 147, 140–156, 2007.
Janssens, I. A., Kowalski, A. S., and Ceulemans, R.: Forest floor CO_2 fluxes estimated by eddy covariance and chamber-based model, Agr. Forest Meteorol., 106, 61–69, 2001.
Kaimal, J. C., Wyngaard, J. C., Izumi, Y., and Cote, O. R.: Spectral characteristics of surface layer turbulence, Quart. J. Roy. Meteorol. Soc., 98, 653–689, 1972.
Kaimal, J. C.: Turbulence spectra, length scales and structure parameters in the stable surface layer, Boundary Layer Meteorol., 4, 289–309, 1973.
Keller, M. and Matson, P. A.: Biosphere-atmosphere exchange of trace gases in the tropics, in: Evaluating the effect of land-use changes, in: Global Atmospheric, Biospheric Chemistry, edited by: Prinn, R. G., Biospheric Chemistry, Plenum, New York, 103–117, 1994.
Keppler, F., Hamilton, J. T. G., Brab, M., and Röckmann, T.: Methane emissions from terrestrial plants under aerobic conditions, Nature, 439, 187–191, 2006.
Keppler, F., Hamilton, J. T. G., McRoberts, W. C., Vigano, I., Bra, M., and Röckmann, T.:

ACPD
11, 5313–5350, 2011

Methoxyl groups of plant pectin as a precursor of atmospheric methane: evidence from deuterium labelling studies, New Phytol., 178(4), 808–814, 2008.
Kiese R, Hewett B, Graham A, and Butterbach-Bahl K.: Seasonal variability of N_2O emissions and CH_4 uptake by tropical rain forest soils of Queensland, Australia, Global Biogeochem., 17(2), 1043–1054, 2003.
Kirschbaum, M. U. F., Bruhn, D., Etheridge, D. M., Evans, J. R., Farquhar, G. D., Gifford, R. M., Paul, K. I., and Winters, A. J.: A comment on the quantitative significance of aerobic methane release by plants, Funct. Plant Biol., 33, 521–530, 2006.
Kirschbaum, M. U. F., Niinemets, Ü., Bruhn, D., and Winters, A. J.: How important is aerobic methane release by plants?, in: Functional Plant Science and Biotechnology, Global Science Books, 138–145, 2007.
Kitaoka, S., Sakata, T., Koike, T., Tobita, H., Uemura, A., Kitao, M., Maruyama, Y., Sasa, K., and Utsugi, H.: Methane Emission from Leaves of Larch, Birch and Oak Saplings Grown at Elevated CO_2 Concentration in Northern Japan – Preliminary Study, J. Agric. Meteorol., 63, 201–206, 2007.
Kljun, N., Rotach, M. W., and Schmid, H. P.: A 3-D backward Lagrangian footprint model for a wide range of boundary layer stratifications, Bound.-Layer Meteorology, 103, 205–226, 2002.
Kroon, P. S., Hensen, A., Jonker, H. J. J., Zahniser, M. S., van 't Veen, W. H., and Vermeulen, A. T.: Suitability of quantum cascade laser spectroscopy for CH_4 and N_2O eddy covariance flux measurements, Biogeosciences, 4, 715–728, doi:10.5194/bg-4-715-2007, 2007.
Kutzbach, L., Schneider, J., Sachs, T., Giebels, M., Nykänen, H., Shurpali, N. J., Martikainen, P. J., Alm, J., and Wilmking, M.: CO_2 flux determination by closed-chamber methods can be seriously biased by inappropriate application of linear regression, Biogeosciences, 4, 1005–1025, doi:10.5194/bg-4-1005-2007, 2007.
Lelieveld, J., Crutzen, P. J., and Dentener, F. J.: Changing concentration, lifetimes and climate forcing of atmospheric methane, Tellus, 50, 128–150, 1998.
Luizão, R. C. C., Luizão, F. J., Paiva, R. Q., Monteiro, T. F., Sousa, L. S., and Kruijt, B.: Variation of carbon and nitrogen cycling processes along a topographic gradient in a Central Amazonian forest, Glob. Change Biol., 10(5), 592–600, doi:10.1111/j.1529-8817.2003.00757.x, 2004.
Malhi, Y. and Davidson, E. A.: Biogeochemistry and Ecology of terrestrial Ecosystems of Amazonia, in: Amazonia and Global Change, Geophysical Monograph Series 186, edited by:

ACPD
11, 5313–5350, 2011

American Geophysical Union, Washington DC, 293–298, 2009.
Malhi, Y. and Grace, J.: Tropical forests and atmospheric carbon dioxide, Trends Ecol. Evolut., 15, 332–337, 2000.
Malhi, Y., Baldocchi, D. D., and Jarvis, P. G.: The carbon balance of tropical, temperate and boreal forests, Plant Cell Environ., 22, 715–740, 1999.
McLeod, A. R., Fry, S. C., Loake, G. J., Messenger, D. J., Reay, D. S., Smith, K. A., and Yun, B. W.: Ultraviolet radiation drives methane emissions from terrestrial plant pectins, New Phytol., 180(1), 124–132, 2008.
Megonigal, J. P. and Guenther, A. B.: Methane emissions from upland forest soils and vegetation, Tree Physiol., 28, 491–498, 2008.
Meirink, J. F., Bergamaschi, P., Frankenberg, C., d'Amelio, M. T. S., Dlugokencky, E. J., Gatti, L. V., Houweling, S., Miller, J. B., Röckmann, T., Villani, M. G., and Krol, M. C.: Four-dimensional variational data assimilation for inverse modeling of atmospheric methane emissions: Analysis of SCIAMACHY observations, J. Geophys. Res., 113, D17301, doi:17310.11029/12007JD009740, 2008.
Messenger, D. J., McLeod, A. R., and Fry, S. C.: The role of ultraviolet radiation, photosensitizers, reactive oxygen species and ester groups in mechanisms of methane formation from pectin, Plant Cell Environ., 32(1), 1–9, 2009.
Miller, J. B., Mack, K. A., Dissly, R., White, J. W. C., Dlugokencky, E. J., and Tans, P. P.: Development of analytical methods and measurements of $^{13}C/^{12}C$ in atmospheric CH_4 from the NOAA/CMDL global air sampling network, J. Geophys. Res., 107, D13, doi:10.1029/2001JD000630, 2002.
Miller, J. B., Gatti, L. V., d'Amélio, M. T. S., Crotwell, A. M., Dlugokencky, E. J., Bakwin, P., Artaxo, P., and Tans, P. P.: Airbone measurements indicate large methane emissions from the eastern Amazon basin, Geophys. Res. Lett., 34, L10809, doi:10.1029/2006GL029213, 2007.
Molion, L. C. B.: A Amazônia e o clima da Terra, Ciencia Hoje, 48(8), 42–47, 1988.
Pattey, E., Strachan, I. B., and Desjardins, R. L.: Measuring nighttime CO2 flux over terrestrial ecosystems using eddy covariance and nocturnal boundary layer methods, Agr. Forest Meteorol., 113, 145–158, 2002.
Prance, G.: Encyclopedia of Biodiversity, Academic Press, 1, 145–157, 2001.
Qaderi, M. M. and Reid, D. M.: Methane emissions from six crop species exposed to three components of global climate change: temperature, ultraviolet-B radiation and water stress,

ACPD
11, 5313–5350, 2011

Physiol. Plant., 137, 139–147, 2009.
Quay, P., Stutsman, J., Wilbur, D., Snover, A., Dlugokencky, E., and Brown, T.: The isotopic composition of atmospheric methane, Global Biogeochem. Cy., 13, 445–461, 1999.
Sanhueza, E. and Donoso, L.: Methane emission from tropical savanna Trachypogon sp. grasses, Atmos. Chem. Phys., 6, 5315–5319, doi:10.5194/acp-6-5315-2006, 2006.
Simon E., Lehamann, B. E., Ammann, C., Ganzeveld, L., Rummel, U., Meixner, F. X., Nobre, A. D., de Araújo, A., and Kesselmeier, J.: Lagrangian dispersion of 222Rn, H_2O and CO_2 within Amazonian rain forest, Agr. Forest Meteorol., 132, 286–304, 2005.
Singh, J. S., Singh, S., Raghubanshi, A. S., Singh, S., Kashyap, A. K., and Reddy, V. S.: Effects of soil nitrogen, carbon and moisture on methane uptake by dry tropical forest soils, Plant Soil, 196, 115–121, 1997.
Smeets, C. J. P. P., Holzinger, R., Vigano, I., Goldstein, A. H., and Röckmann, T.: Eddy covariance methane measurements at a Ponderosa pine plantation in California, Atmos. Chem. Phys., 9, 8365–8375, doi:10.5194/acp-9-8365-2009, 2009.
Steudler, P. A., Melillo, J. M., Feigl, B. J., Neill, C., Piccolo, M. C., and Cerri, C. C.: Consequence of forest-to-pasture conversion on CH_4 fluxes in the Brazilian Amazon Basin, J. Geophys. Res., 101(18), 547–554, 1996.
Tóta, J., Fitzjarrald, D. R., Staebler, R. M., Sakai, R. K., Moraes, O. M. M., Acevedo, O. C., Wofsy, S. C., and Manzi, A. O.: Amazon rain forest subcanopy flow and the carbon budget: Santare'm LBA-ECO site, J. Geophys. Res.-Biogeo, 113(15), G00B02, doi:10.1029/2007JG000597, 2008.
Tuzson, B., Hiller, R. V., Zeyer, K., Eugster, W., Neftel, A., Ammann, C., and Emmenegger, L.: Field intercomparison of two optical analyzers for CH_4 eddy covariance flux measurements, Atmos. Meas. Tech. Discuss., 3, 2961–2993, doi:10.5194/amtd-3-2961-2010, 2010.
Veldkamp, E., Keller, M., and Nunez, M.: Effects of pasture management on N_2O and NO emissions from soils in the humid tropics of Costa Rica, Glob. Biogeochem. Cyc., 12, 71–79, 1998.
Vesala, T., Kljun, N., Rannik, U., Rinne, J., Sogachev, A., Markkanen, T., Sabelfeld, K., Foken, T. H., and Leclerc, M. Y.: Flux and concentration footprint modelling: State of the art, Environ. Pollut., 152, 653–666, 2008.
Verchot, L. V., Davidson, E. A., Cattânio, H. J., and Ackerman, I. L.: Land-use change and biogeochemical controls of methane fluxes in soils of eastern amazonia, Ecosystems, 3, 41–56, 2000.

ACPD
11, 5313–5350, 2011

Vigano, I., van Weelden, H., Holzinger, R., Keppler, F., McLeod, A., and Röckmann, T.: Effect of UV radiation and temperature on the emission of methane from plant biomass and structural components, Biogeosciences, 5, 937–947, doi:10.5194/bg-5-937-2008, 2008.

Vigano, I., Holzinger, R., Röckmann, T., van Dijk, A., Keppler, F., Greule, M., Brand, W. A., van Weelden, H., and van Dongen, J.: UV light induces methane emission from plant biomass: Mechanism and isotope studies, Geochim. Cosmochim. Acta, 73(13), A1382–A1382, 2009a.

Vigano, I., Röckmann, T., Holzinger, R., van Dijk, A., Keppler, F., Greule, M., Brand, W. A., Geilmann, H., and van Weelden, H.: The stable isotope signature of methane emitted from plant material under UV irradiation, Atmos. Environ., 43(35), 5637–5646, 2009b.

Vigano, I., Holzinger, R., Keppler, F., Greule, M., Brand, W. A., Geilmann, H., van Weelden, H., and Röckmann, T.: Water drives the deuterium content of the methane emitted from plants, Geochim. Cosmochim. Act., 74, 3865–3873, 2010.

Wang, Z. P., Han, X. G., Wang, G. G., Song, Y., and Gulledge, J.: Aerobic methane emission from plants in the Inner Mongolia steppe, Environ. Sci. Technol., 42, 62–68, 2008.

Wang, Z.-P., Gulledge, J., Zheng, J.-Q., Liu, W., Li, L.-H., and Han, X.-G.: Physical injury stimulates aerobic methane emissions from terrestrial plants, Biogeosciences, 6, 615–621, doi:10.5194/bg-6-615-2009, 2009.

Wienhold, F. G., Welling, M., and Harris, G. W.: Micrometeorological measurements and source region analysis of nitrous oxide fluxes from an agricultural soil, Atmos. Environ., 29(17), 2219–2227, 1995.

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11, 5313–5350, 2011

Table 1. 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}

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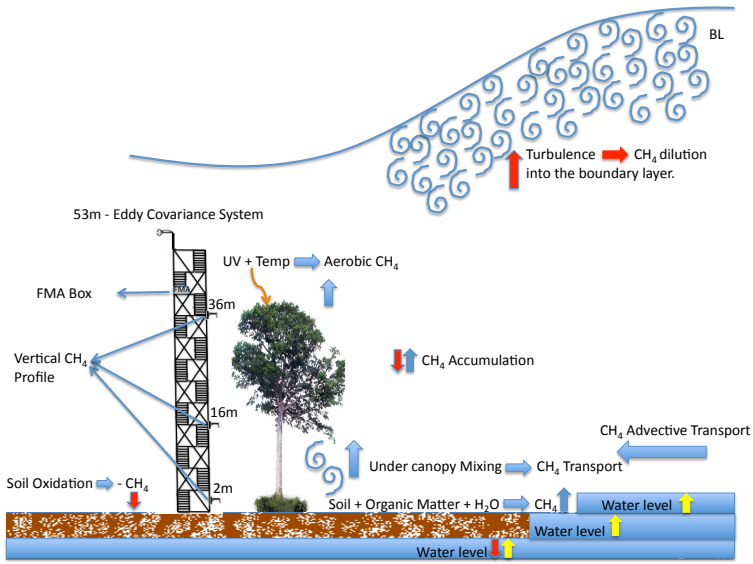

Fig. 1. Schematic picture of the measurement equipment installed at the K34 tower, in combination with processes that influence CH_4 levels below and above the canopy in the tropical forest environment. 06 h integrated samples are taken at levels, near the ground (2 m), close to the top of the canopy (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. In a well aerated (dry) soil, CH_4 can also be removed and taken up from the atmosphere. UV radiation and temperature have been shown to induce CH_4 emissions from fresh and dry organic matter (Vigano et al., 2008), but emissions from living plants have not been unambiguously identified. 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.

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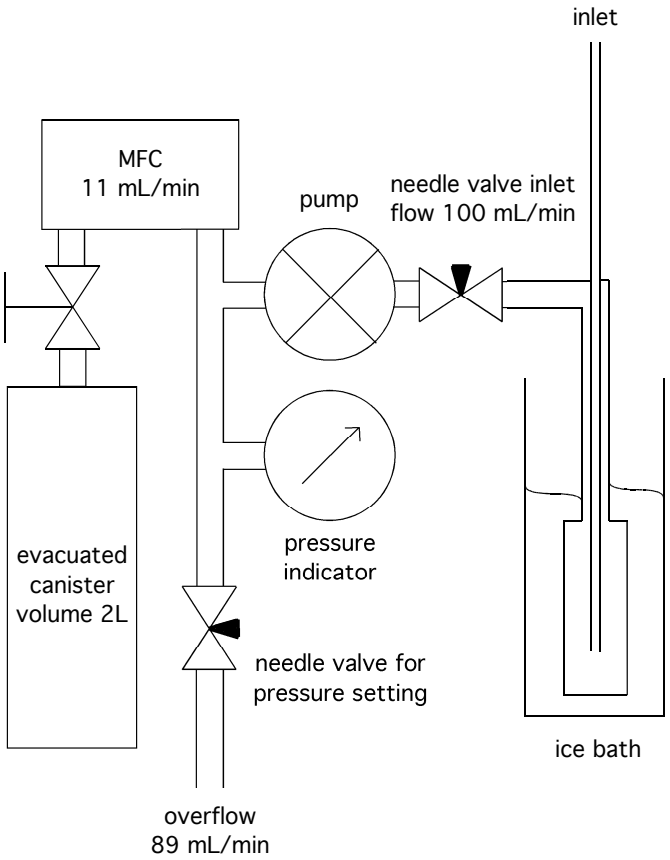

Fig. 2. Schematic drawing of the gradient air sampling units. In the first stage, the air passes for an ice bath to dry the air sample. Afterwards it is flushed to inside an evacuated canister (2 L). Controlled by a Mass Flow Control (MFC) the flow ratio is regulating in 11 mL min^{-1}. Typically samples were taken over a period of 6 h.

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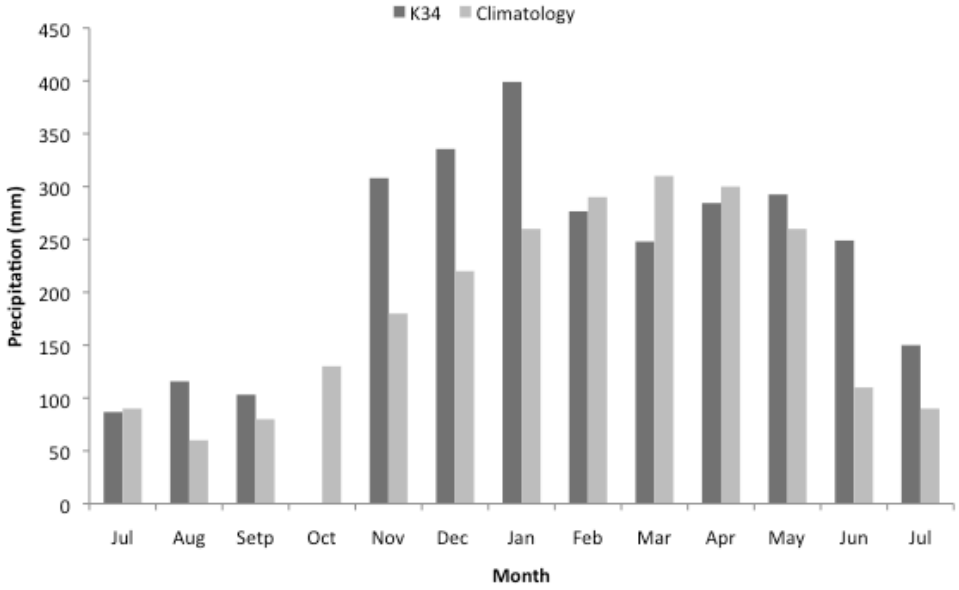

Fig. 3. Comparison between K34 rainfall data from July 2008 to July 2009 and the Manaus climatologically mean. Due to technical problems the data of October 2008 are not available.

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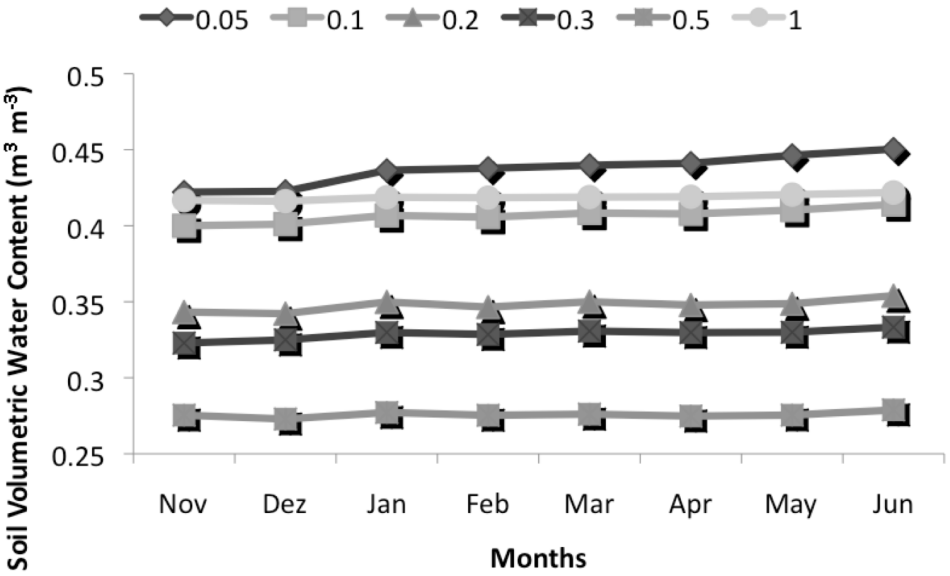

Fig. 4. Monthly average of the soil volumetric water content at six different levels below the surface (in meters) from November 2008 to June 2009.

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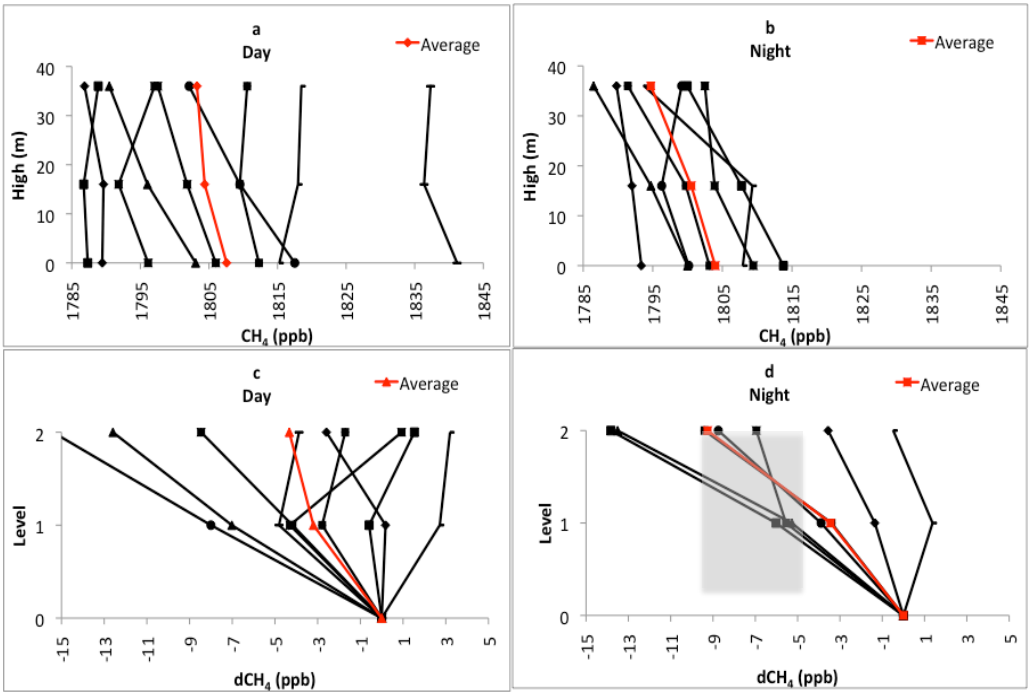

Fig. 5. Diurnal and nocturnal vertical gradient measurements. **(a)** and **(b)** individual CH_4 mixing ratios and **(c)** and **(d)** ΔCH_4 relative to the 2 m level within the forest. The grey-shaded area in **(d)** corresponds to the average CH_4 excess that is exchanged per hour from the canopy according to the calculations in Sect. 4.3.

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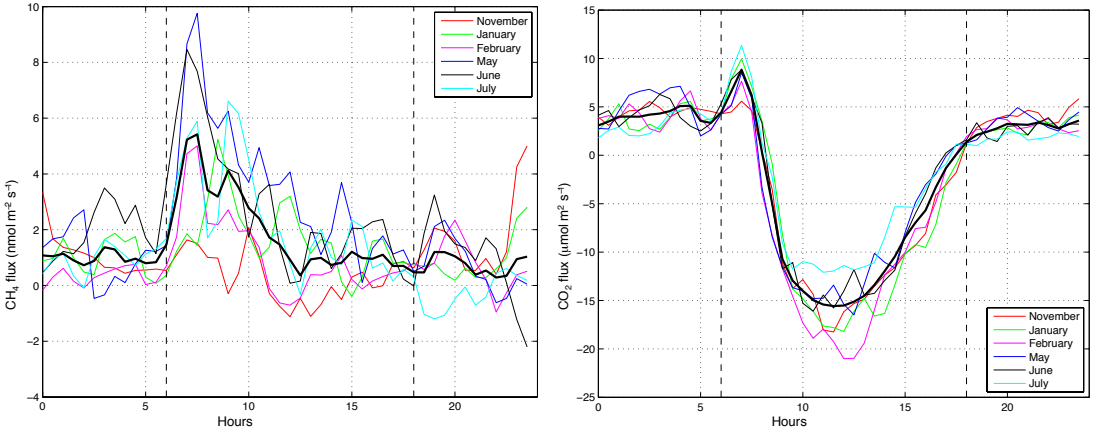

Fig. 6. Monthly averaged diurnal cycles of CH_4 **(a)** and CO_2 **(b)** fluxes measured in a tropical forest.

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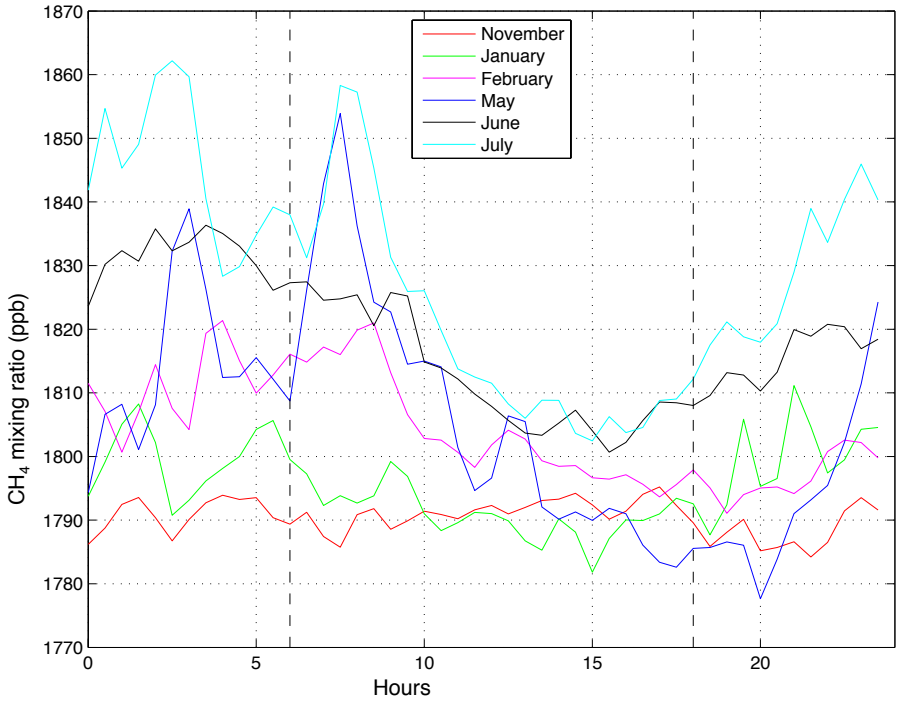

Fig. 7. Monthly averaged diurnal cycles of CH_4 mixing ratios measured with the FMA at the top of the tower K34 during six months. Vertical dashed lines indicate the time of sunrise and sunset, respectively.

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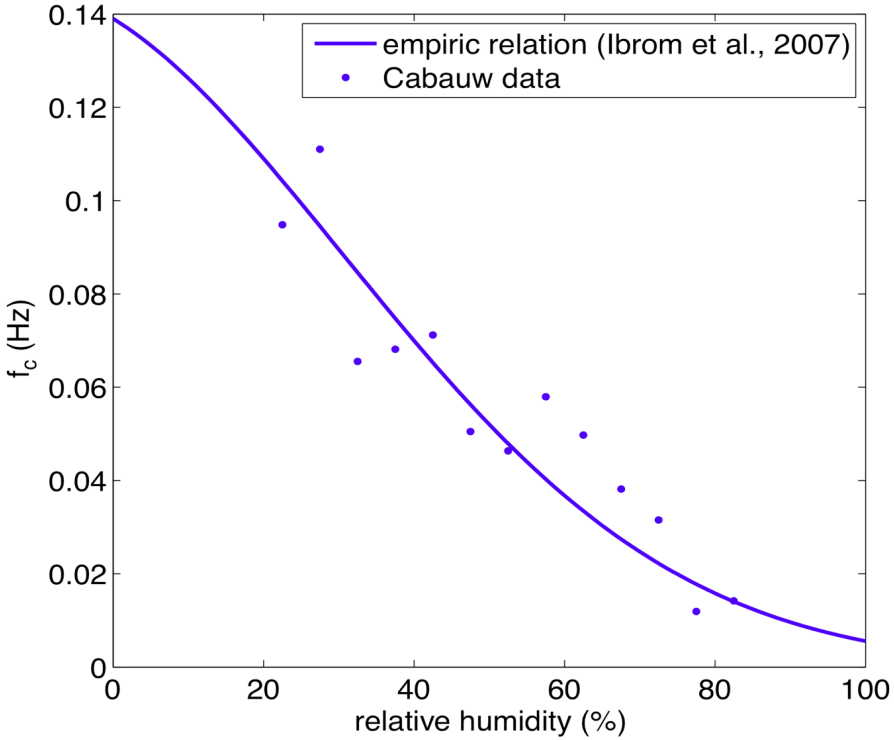

Fig. 8. Cut-off frequency for water vapor as a function of relative humidity. The various symbols are the results from combining different fits to the spectra and various data selection criteria applied to the Cabauw data. The solid line represents the empirical model presented by Ibrom et al. (2007).

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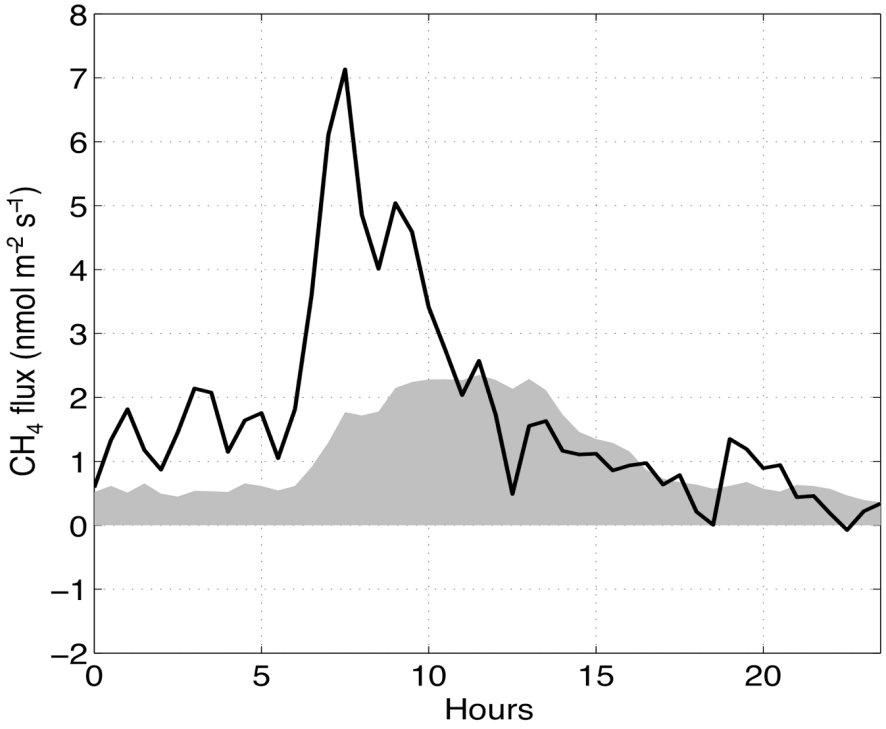

Fig. 9. Averaged diurnal variations of methane fluxes (solid line) and the corresponding detection limit (filled area) for data obtained from January to July 2009.

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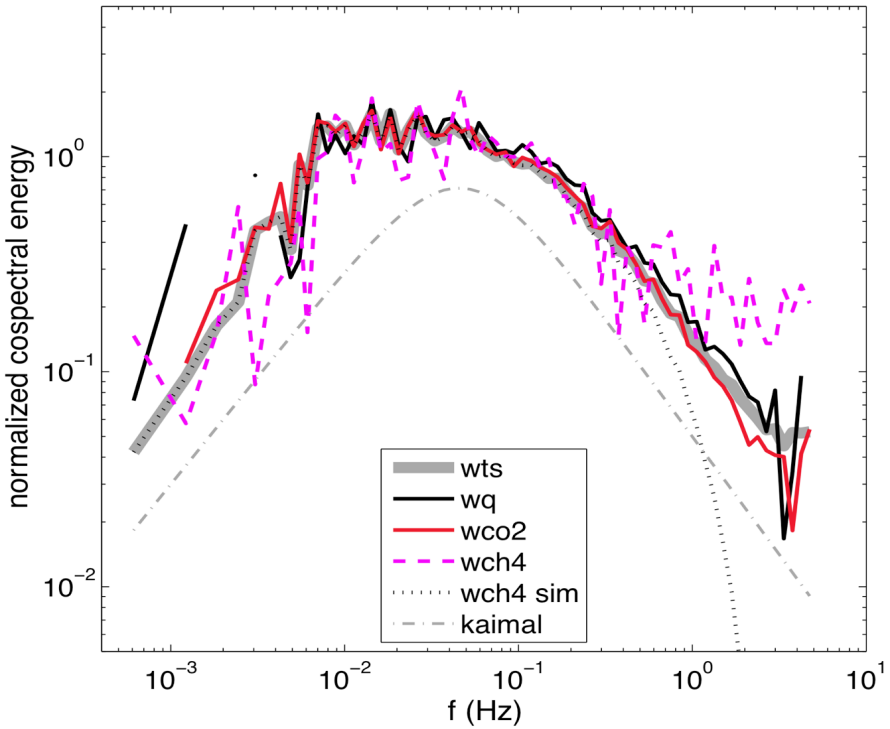

Fig. 10. Normalized averaged co-spectra from an ensemble of 109 half hour nighttime runs obtained between 20:00 and 05:00 h from February to July 2009. The co-spectra for sonic temperature, water vapor, CO_2 and CH_4 flux are plotted as a function of natural frequency. The dotted black curve (CH_4 simulated) 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 $\overline{u} = 2.2 \pm 0.6\,\mathrm{m\,s^{-1}}$.

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