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Atmospheric
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Interactive comment on "Methane emissions from boreal and tropical forest ecosystems derived from in-situ measurements" *by* V. Sinha et al.

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We thank the anonymous reviewer for his/her helpful and insightful remarks.

Before addressing the comments of the reviewer in detail, at the very outset, it is worth re-iterating that with regard to the diel trends in the methane mixing ratio, especially the nighttime increase within the canopy of forest ecosystems, Carmo et al. (2006) and Crutzen et al. (2006) have also previously reported similar methane profiles, which capture the nighttime increase in methane mixing ratios with different instrumentation and sampling techniques, to that used in the present study. The uniqueness of the present study lies in 1) the improved temporal resolution of the methane profiles 2) the fact that with the same instrument and in the same year we analyzed methane emissions from two different forest ecosystems, thus enabling a direct comparison of methane profiles. Note also, that recent works on methane (e.g. by Frankenberg et al.(2005) and Bergamaschi et al.(2007), have repeatedly highlighted the need for more in-situ methane data from forested site since the current dataset is rather sparse.

The major concern of the reviewer pertains to whether the measured diel profiles of methane are ”real ” or an instrumental ”artifact”. We agree with the reviewer that more details regarding the instrumental diagnostics and data quality would be helpful for readers and we shall certainly include them in the revised version. Table 1 shown herein lists some of the monitored instrumental parameters along with their average, median and standard deviation. These instrumental parameters were logged for each measurement (every 70 seconds) (raw data) and include: 1) temperature of the detector oven, 2) temperature of the column oven, 3) temperature of the column air 4) the fuel (H2), carrier gas (N2) and synthetic air pressures, 5) methane peak retention time (R.T.). Clearly, all of them were very stable and thus the possibility of erratic instrumental performance (due to these parameters) producing an ”artifact” diel cycle can be totally ruled out.

Table 1

	Det. Oven	Col. Oven	Col. Air	H2	Syn Air	N2	CH4 R.T.
Units	°C	°C	°C	PSI	PSI	PSI	s
Mean	176.2	72.4	66	37.5	29	29	11.97
Median	176	72	66	37	29	29	12
Std.dev	1.6	0.7	0.9	0.5	0.6	0	0.07

Detailed below are replies (R) to the more specific concerns (C) raised by the reviewer. Specific comments:1.

C) How was the sample air dried?

R) The sample air was not dried and neither was the ambient air subject to any preconcentration. The flame ionization detector is not sensitive to water so changes in ambient humidity levels do not affect instrument performance. In addition, the chromatography is optimized to prevent interference from the water peak. To be doubly sure that the ambient air humidity fluctuations do not impact the methane measurements the correlation between the RH content of the ambient air and the measured methane mixing ratios was also investigated and no correlation was seen ($r^2 = 0.14$; Figure 1 http://www.atmosphere.mpg.de/enid/figures-sinha.

C) How was the pressure of the GC sample loop controlled? What was its volume? Was the temperature controlled?

R) The internal pump of the instrument sucks in 1.2 L/min. Frequent flow measurements done manually showed this flow to be constant during the campaign. Even so, a pump solenoid within the instrument, stops sample flow prior to sample injection. This eliminates oscillation from the pump and equilibrates the sample loop to ambient at every injection. Changes in ambient pressure have no impact (r^2= 0.15 for correlation between the ambient air pressure and methane mixing ratio ; Figure 2 http://www.atmosphere.mpg.de/enid/figures-sinha. This new figure will be included in the revised version.

The sample loop volume was 2.0cc. The sample loop and rotary valve are located inside an oven operating at 176 °C. The column is located in a different oven operating at 66 °C. As already mentioned, the temperature of both the detector oven, the column oven as well as the column air was monitored (Table 1), and found to be quite stable.

C) Was the detector linearity tested or assumed over the range from ambient CH4 to the 4 ppm standard?

R) The linearity of the detector signal of the instrument was tested for the range 0.5 ppmV - 4 ppmV. The linearity was very good (r^2= 0.98) and in the revised version, we shall include the new plot showing the linearity of the detector (Figure 3 at http://www.atmosphere.mpg.de/enid/figures-sinha.

C) How was the instrument response calibrated? At what frequency?

R) In addition to prior calibrations as mentioned above, the instrument was calibrated during the field measurements using a 3.96 ppmV methane gas standard (Westfalen AG, stated accuracy 2%). It should be noted that the instrument stores the most recent calibration factor. In the field, first the calibration gas was introduced as sample air and the measured value noted (multiple readings were taken of course). This enabled us to determine the response factor drift compared to the last calibration, and this was never found to be more than 0.2% at the methane mixing ratio of 3.96 ppmV. Next, the calibration gas (3.96 ppmV methane) was introduced again, and the new response factor set. Thus throughout the period of our measurements, the response factor of the instrument never drifted by more than 0.3%.

C) What GC column packing was used.? R) This is a special proprietary column that has been developed by the Thermo electron Corporation, MA for direct methane measurements of ambient air.

C) Why is the quoted precision, 2%, much greater than what is typically obtained with a GC system?

R) The instrument has an auto calibration function whereby calibrations are performed automatically at specified time intervals. We did not choose this option because we never found the drift in the response factor to be more than 0.2 %. Still, as the instrument manual states that not using the auto calibration function can cause a drift of up to 2%, we chose to report the worst case scenario.

Specific comments 2: C) What quality control and quality assurance procedures were used to insure that the measurements are reasonable? A plot of CH4 mixing ratios, either raw data or 15 min averages, should be presented for 1 day to give readers a feel of instrument variability.

R) For quality control, all measurements less than 1.5 ppmV and greater than 2.5 ppmV were rejected. This rejected dataset is less than 0.09 % of the total measured dataset which exceeded 10,000 measurements. Furthermore, the inlet was placed at the canopy height and far from direct potential methane sources such as termite hives in the tropical forest. We appreciate the Reviewer8217;s point and raw data (Figure 4 http://www.atmosphere.mpg.de/enid/figures-sinha)(15 min average) as asked, will be included in the revised version.

C) These measurements should be compared with measurements from other programs for comparable latitudes. The low end of the measurement range at Brownsberg is significantly lower than CSIRO measurements of CH4 at Cape Grim at high southern latitudes. This could not be correct. Could errors in the standard be responsible for the entire difference?

R) We thank the reviewer for this nice suggestion. Following up on it, has indeed shown that our measurements compare well with measurements at the Pallas station in Finland (Aalto et.al., 2007). When compared to data from this site shown in Fig. 2 and Table 1 of Aalto et al. (2007), which shows the monthly mean data for April, 2005 (the same month and year as our measurements) the value is 1868 ppbV, which is quite close to our reported average from Hyytiäla of 1830 ± 38.5 ppbV. This will be noted in the revised version.

With regard to the comment of the reviewer that the low end of our measurement at Brownsberg (approx. 1678 ppbV in Fig 4 of the manuscript) is less than the typical mean value of approx. 1710 ppbV for the same period at Cape Grimm, (http://cdiac.ornl.gov/trends/atm_meth/csiro/csiro-cgrimch4.jpg) and (http://www.dar.csiro.au/capegrim/image/cg_CH4.png), we note that first of all the Cape Grimm data is a monthly average (October) while the low end of our measurements are the 5-95 percentiles. Thus strictly speaking, one should not compare the two values, because the lower range of the Cape Grimm measurements will also be less than the average of approx. 1710 ppbV.

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Nevertheless, we have still heeded the suggestion of the reviewer. Taking into account the overall uncertainty for the values in Fig 4 of the manuscript, which is 2.1% ($\sqrt{(2^2} + 0.6^2$) the lower range of the Brownsberg value together with its uncertainty is 1678 $\pm$ 35 ppbV. We shall duly note that the low end of the measurements at Brownsberg are comparable to the average monthly methane mixing ratios for October at Cape Grimm, in the revised version of the paper.

C) At Brownsberg, there is significantly less variability between 1400 and 1630 than at other times; why does it change so abruptly during this period? After 1630, the range of observations is very asymmetric; why?

R) Due to the incomplete meteorological dataset at Brownsberg (data only available from 26-31August, 2005 and 1-5 October, 2005, before software problems between the tower based sensors and the control computer caused a breakdown) we have deliberately refrained from interpreting the Brownsberg methane diel cycle in detail. Based on the dataset from 26-31August, 2005 and 1-5 October, 2005 (personal communication Dr. Bert Scheeren 2006) it is clear that the Brownsberg site has a very specific meteorology at 14:00 LT, which is characterized by the slowing down of the wind speed (from 3m s^{-1} to 2 m s^{-1}) and an abrupt change in wind direction from 135°(SE) to 250°(SW). Thus during the period from 1400 to 16:30 the low variability is very likely due to the change in the prevailing wind direction at the site and hence the fetch area. Shortly after 1630, the wind direction resumes its SE direction again.

By " asymmetric ", we assume that the reviewer implies that from 16:30 to 20:30 LT, the mean and median values diverge, with the mean being higher. During the campaign, it was noticed that residents at the Brownsberg Nature Reserve lighted up their wood based cooking stoves, which were located outdoors at around 17:00 hours. Thus, during this period there was some local methane emission, and therefore the mean values which are sensitive to outliers diverge from the medians. Note however that the cooking activity at this otherwise remote site occurred only for a few hours and for the flux discussion, we have only used the median nighttime values from the profile.

3. Flux calculation:

C) The lack of vertical gradient in CO2 at night does not convince me, because I do not know the CO2 flux. Could it be very small at this time of year? For a significant flux of CH4 or CO2, I would still expect a gradient within the NBL because, at such low wind speeds, mixing would be slow.

R) We thank the reviewer for raising this important and valid point.

First of all, we note that the Hyytiäla forest site has evergreen trees, so that leaf respiration by the vegetation at night would still result in CO2 release. Secondly our measurements were conducted in April-May which typically marks the onset of the growing season, and not in winter which has the lowest biological activity. Thirdly Figure 2 and Figure 3 in Suni et al.(2003) clearly show that for April-May, the nighttime CO2 flux at this site is typically 20 g m^{-2} (taking the average of the nighttime CO2 flux in Spring for all the years from 1997-2001). Also taking into account that the average length of Spring for the years 1997-2001, was 45 days (Suni et al., 2003), this amounts to a nighttime CO2 flux of 7 x 10^{12} molecules cm^{-2} s^{-1}, considerably higher than the nighttime CH4 flux, derived in our study. The vertical profile of CO2 mixing ratios do show a weak logarithmic profile and this has now been taken into account for the deriving a more accurate flux in the revised version (see Figures 5 and 6 at http://www.atmosphere.mpg.de/enid/figures-sinha). Please also see reply to Bergamaschi et al. (2007b) in this interactive discussion.

C) Is the calculated Boreal flux consistent with the work of Bergamaschi et al. (ACP, 5, 2431-2460, 2005) where very low CH4 fluxes are reported for Finland?

R) We have already compared our Boreal flux data with the more recent work of Bergamaschi et al. (2007), wherein methane emission fluxes for the year 2003 have been reported. Bergamaschi et al.(2005) investigated countrywide emissions in Europe for the year 2002 and we do not think it is appropriate to compare emissions from a boreal forest ecosystem (our work) and emissions from the entire country of Finland consist-

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ing of diverse natural and anthropogenic sources, especially when the country wide emissions are expressed in Tg yr^{-1} (Table 1, Bergamaschi et al., 2005).

C) Could variations in atmospheric pressure and temperature through the night systematically affect the conversion factor used to go from mixing ratio to number density?

R) The conversion factor (C.F.) (nmol mol^{-1} to molecules cm^{-1}) is a function of the ambient pressure and temperature (P,T), such that C.F is directly proportional to the ratio of P/T for a fixed quantity of the gas (moles). During the period of our measurements, the pressure and temperature differences between 20:00 and 06:00 in Hyytiäla were never more than 4.4 mbar and 8°, respectively and these extreme changes in the temperature and pressure did not occur simultaneously. The average pressure and temperature differences (absolute values) between 20:00 and 06:00, were only 1.3 mbar and 5.7°. Taking the case of the night when the temperature changed by circa 8°C, we show below the C.F change during the course of the night.

At 20:00 LT the ambient pressure and temperature was (993.6,7.69) and the corresponding conversion factor was 2.56 x 10^{10} molecules cm^{-3}.The following morning at 06:00 LT, the ambient pressure and temperature was (994.06,-0.37), and the corresponding C.F. was 2.64 x 10^{10} molecules cm^{-3}. Both values differ only slightly from the C.F. of 2.69 x 10^{10} molecules cm^{-3}, actually used for the flux calculation. Still, if we plug in the respective C.F. values into the flux calculation (Equation 1 of the manuscript), the calculated flux changes by less than 0.3%, and clearly, even for this worst case scenario, the calculated flux is not affected significantly.

4.

C) Tropical measurements: Given the relatively large uncertainties in these measurements, the SCIAMACHY column averages, and the TM3 results, even qualitative statements about tropical fluxes may not be appropriate.

R) We respectfully disagree with the Reviewer. Inter comparing measurements and

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calculated fluxes obtained using different methods is a very helpful way of 1) constraining the potential source/sink contributions 2) understanding the advantages and limitations intrinsic to different methodologies. Thus, it is reasonable to make qualitative statements about measurements obtained using different methods. Regarding the specific discussion of the tropical flux, as both reviewers have concerns about it, we shall not include it the revised version.

5.

C) CH4 emissions from vegetation: I am not sure that 10 days of measurements at one site in Finland extrapolated to the entire Boreal region add much new to our understanding of CH4 emissions from vegetation. How can these results be reconciled with the work of Dueck et al.?

R) Our work employs in-situ measurements from the forest ecosystems to assess the potential impact of vegetative emissions. All previous works on vegetative emissions (Keppler et al.,2006; Dueck et al.,2007; Houweling et al., 2007) have been based on either extrapolation of laboratory data or models, even though the mechanism of methane production from plants is not known. As noted in the manuscript (Section 4.1), the in-situ measurements suggest that the contribution of boreal vegetation to the total methane budget is at best very small, and within the uncertainty of the known sources. Such a result is not irreconcilable with Dueck et al. (2007), whose laboratory based study indicated no significant methane emissions from plants, under aerobic conditions.

Technical comments:

In the revised version we will incorporate the recommended changes. In particular, we are grateful to the Reviewer for highlighting an oversight regarding the total uncertainty of the measurements, which had been overestimated in the manuscript and will change from 2.58% as reported earlier, to 2.1% (applying the rule of error propagation)

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We hope that this reply has allayed fears about the reported diel profiles being an experimental ”artifact” and we thank the Reviewer for her/his comments, that have strengthened the manuscript.

References

Aalto, T., Hatakka, J., and Lallo, M.: Tropospheric methane in northern Finland: seasonal variations, transport patterns and correlations with trace gases, Tellus, 59B, 251-259, 2007.

Bergamaschi et al.: Interactive Comment on Methane Emissions from Boreal and Tropical Forest Ecosystems, Atmos. Chem. Phys. Discuss., 7, S58928211;S5895, www.atmos-chem-phys-discuss.net/7/S5892/2007/, 2007

Suni, T., F. Berninger, T. Markkanen, P. Keronen, U. Rannik, and T. Vesala: Interannual variability and timing of growing season CO2 exchange in a boreal forest, J. Geophys. Res., 108(D9), 4265, doi:10.1029/2002JD002381, 2003

Other references can be found in the ACPD manuscript

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 14011, 2007.