Atmos. Chem. Phys. Discuss., 10, C2568–C2574, 2010
www.atmos-chem-phys-discuss.net/10/C2568/2010/

Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on "Fluxes and concentrations of volatile organic compounds from a South-East Asian tropical rainforest" *by* B. Langford et al.

Anonymous Referee #1

Received and published: 11 May 2010

The paper describes ecosystem scale VOC emissions from South-East Asian rainforest measured by disjunct eddy covariance method. As the tropical rainforests are a major source of reactive VOCs into the atmosphere, and as pointed out by the authors, the measurement data from these regions is still scarce, there is need for such a data. Especially important this is for evaluation of emission models in these regions. The methodology of the paper and conclusions drawn from results are mostly sound. The conclusions are not entirely new but they add important information on the performance of commonly used models in this globally important region. I propose acceptance of the paper after considering the following comments.

Page 11977, line 8: “There is evidence that isoprene also contributes to BSOA formation. . .” Maybe the authors should mention that there is also evidence on the contrary as well (Kiendler-Scharr, et al., 2009: New particle formation in forests inhibited by isoprene emissions. Nature, 461 (7262), 381-384).

Page 11979, lines 16-22: The description set-up needs some refinement. What was the inner diameter of the main sample line? Only outer diameter is given in the paper. Also, flow rate in the main line is not given in the paper. How short was the short length of 1/8” OD tubing from main line to the PTR-MS? What was the inner diameter of this tube?

Page 11980, lines 24-25: “For those compounds not contained in the gas mixture, empirical sensitivities were calculated based on the instrument-specific transmission characteristics. . .” How was the transmission curve determined? Normally one needs calibration with non-fragmenting compounds at higher masses to interpolate the transmission curve values. In the standard mixture described in the paper no such compound was present. Also, the authors should specify how the monoterpene concentrations we determined. Were they determined from m/z 81 or 137 or both and what fragmentation was assumed? The conclusions on quantitative results given in the paper require the quantification of the VOC concentrations to be reliable.

Pages 11981, line 7 - page 11982, line 9: Chapter “2.2 PTR-MS operation and flux calculations” More detail should be given on the lag-time detection. Was the lag-time detection done automatically or subjectively? How about using the method proposed by Taipale et al. (2010), already cited in the paper?

Page 11982, line 26: “. . .cannot resolve fluctuations in the sub 0.2 s range. . .” The authors have mentioned above (Page 11981, line 13) that dwell time of 0.5 seconds was used. Thus the measurement system cannot resolve fluctuations faster than that, and not 0.2 s as stated in the paper. Also the long measurement line can include further dampening of high frequencies.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

Page 11982, line 27 - page 11983, line 2: “In contrast, the low frequency flux losses, arising from insufficient averaging periods, were more significant, as shown by Fig. 1. For a detailed description of the method, see Langford et al. (2010)” and Figure 1 with its caption. More explicit description is needed here. Especially Figure 1 is hard to understand with current caption.

Page 11984, lines 3-5: “It should be noted that the PTR-MS LE fluxes are in fact sampled disjunctly, which, when coupled with (i) the indirect calibration against the closed-path IRGA and (ii) the greater uncertainty associated with lag time analyses of disjunctly sampled data (Taipale et al., 2010), may account for the larger disparity between the measurement systems.” I agree that calibration issues may explain the systematic error. However, the greater uncertainty should not create bias to the flux, just add uncertainty.

Page 11984, lines 6-8: “These analyses suggest that VOC fluxes measured at this site are underestimated due to both insufficient averaging periods and some signal attenuation along the 75m sampling line, but the flux loss is unlikely to exceed 30% for any compound”. One source of systematic error in ecosystem emission rates measured by above canopy flux techniques is the chemical reactions below measurement height (e.g. Strong et al., 2004: Reactive hydrocarbon footprints during canopy senescence, Agric. For. Meteorol., 127, 159–173; and Rinne et al., 2007: Hydrocarbon fluxes above a Scots pine forest canopy: measurements and modeling. Atmos. Chem. Phys., 7, 3361-3372). This was not discussed in the paper even though measurements were conducted higher above the canopy than in many other BVOC flux experiments. Could the mode CiTTyCAT, already applied to interpret the data of the paper, be used to address this issue?

Page 11984, lines 19-20: “For methanol, instrument background counts were unusually high, resulting in a very high detection 20 limit of 1.2 ppbv”. Was the variation of this background also high to have this high detection limit?

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

Page 11985, lines 16-18: “Over the course of a typical day, the (MVK+MACR)-to-isoprene ratio shows a distinct pattern, with a sharp decline observable at dawn as the nocturnal ratio decreased from 0.36 to 0.1 in the early morning”. As there is no Figure of MVK+MACR to isoprene ratio it is hard for a reader to judge this.

Page 11985, lines 20-22: “As the isoprene emissions are transported away from the canopy they react to form more MVK+MACR and thus the ratio increases steadily throughout the day. . .” This explanation is not very well formed as the measurements were conducted all the time at the same distance from the isoprene source. I believe that even in well mixed conditions (such as a box model) with constant isoprene source the MVK+MACR to isoprene ratio would increase with time due to accumulation of these reaction products. Of course after sufficiently long time in such conditions an equilibrium would be reached.

Page 11987, line 6: “. . .temperature-dependent plant emitters. . .” Is it expected that there are any? In the absence of significant terpenoid storage in the plant the emissions are likely to follow closely the synthesis (Grote R. & Niinemets Ü. 2008: Modeling volatile isoprenoid emissions – a story with split ends. Plant Biol. 10, 8–28; Loreto et al. 1996: Evidence of the photosynthetic origin of monoterpenes emitted by Quercus ilex L. leaves by 13C labeling. Plant Physiol. 110, 1317–1322; Ghirardo et al. 2010: Determination of de novo and pool emissions of terpenes from four common boreal/alpine trees by 13CO2 labeling and PTR-MS analysis. Plant Cell Environ., 33, 781-792). The broadleaved plants common in tropics do not often have such storages and thus it is unlikely that there is any significant temperature-only-dependent emission.

Page 11987, lines 7-12: “In contrast, early morning emissions of both isoprene and monoterpenes that accumulated in the shallow nocturnal boundary layer were occasionally observed as large spikes at around 08:00–09:00 during the break up of this stable air. However, in-canopy gradient measurements of these compounds during OP3-III showed that both compounds did not build up inside the canopy during the night and that dark emissions were negligable (Ryder et al., 2010)”. It is hard for the reader to judge these flux spikes from the figures. Maybe an additional figure showing examples would help. The paper makes a few references on the morning "venting" events further down the text (e.g. page 11988, lines 10-11 and page 11992, lines 1-2). However, here it seems to conclude that there is no accumulation. Perhaps the authors should be a bit more consistent on their opinion on this issue.

Page 11989, line 16 – page 11990, line 10. The fitting of the G06 algorithm to the flux data ignores the effect of light attenuation within canopy on the functional form of the PAR response. Thus I would refrain from adjusting the functional form of the algorithm based on this analysis even though the ecosystem scale base emission rates based on the flux data can be useful on modeling purposes.

Page 11990: lines 23-25: "Model estimates using the standard coefficients compare reasonably well with measured values, confirming temperature and light to be the primary drivers of observed emissions". Even though I believe this conclusion is a correct one it is not well founded here. As the algorithm used is light saturated in the daytime conditions, it responses only to temperature. Thus it may be difficult to conclude which algorithm, the temperature-only-dependent evaporative emission algorithm, or the temperature-and-light-dependent synthesis emission algorithm.

Page 11990, line 26 – page 11991, line 1: "On 9–10 July, measured VOC fluxes peak in the morning, 2–3 h earlier than the modelled output". This is hard to see from the Figures. Page 11991, lines 17-20: "In contrast, optimization of the temperature response based on monoterpene fluxes showed no deviation from the standard G06 response. This is not unexpected due to the light dependent nature of the monoterpene emissions reported at this site (Ryder et al., 2010)". To me it is not clear why the monoterpene emission should follow more closely the G06 algorithm than isoprene emission, for which it is actually developed for.

Page 11992, line 12 – page 11994, line2: Chapter "3.2.3 Fluxes of other BVOCs". As a general question on this chapter: were these fluxes in general statistically significantly

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

different from zero?

Page 11996, lines 8-10: “Combined with the evidence from in-canopy measurements, these data demonstrate that monoterpenes were not emitted at night and during the day they were found to be dependent on both light and temperature”. I guess this could be expected. The authors could take one step further and discuss the biology of the monoterpene emissions in light of the 13C labeling experiments on monoterpene emissions and inspired by a recent paper by Niinemets et al., (The emission factor of volatile isoprenoids: caveats, model algorithms, response shapes and scaling, Biogeosciences Discuss., 7, 1233–1293, 2010).

Technical comments

Page 11978, line 10: “. . .alsobenchmark. . .” should be “. . .also benchmark. . .”

Page 11986, line 17: “Figures 4 and 4. . .” should be Figures 4a and 4b. . .”

Page 11989, line 8: “. . .0.23 ± 0.3. . .” There are too many significant figures in this value. A common practice is not to express any numeric value more accurately than it can be determined. Thus in this case the value of the ratio should be expressed as 0.2 ± 0.3. In many occasions in the paper the measured values are given with three significant figures (e.g. page 11987, line 16 1.85 mg m-2 h-1, and a few other emission values in the same page, many mixing ratio values in Table 2a and flux values in Table 2b). This would indicate the uncertainty of these values to be less than 10 %, which I doubt. I would prefer using only two significant figures.

The Table 3 nicely reviews information on VOC emission measurements conducted in tropical rainforest. Paper by Müller et al. (2008: Global isoprene emissions estimated using MEGAN, ECMWF analyses and a detailed canopy environment model. Atmos. Chem. Phys., 8, 1329–1341) has also isoprene flux data from the Amazon region. This paper deals with modeling of isoprene by MEGAN, thus it is surprising to see it missing.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

Many of the Figures are not very clear:

Figure 1 has insufficient caption. It is hard to understand the message of the figure. Figure 2 a could be more clear if the lines would have markers. Now it is hard to trace the fluxes as many lines are vertical. Figures 4 a and b have too much data to be informative. One cannot see the shapes of diurnal fluxes. The message of Figure 6 could be better conveyed with model vs measurement plots.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 11975, 2010.