We would like to thank Reviewer #1 for their careful and thorough appraisal of our manuscript. We have addressed each comment in turn below.

RC: Reviewer comment.
AR: Authors response.

RC: 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).

AR: A comment mentioning the findings of Kiendler-Scharr et al., (2009) will be added.

RC: 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?

AR: The ID of the main inlet line was 0.38" and the flow rate was approximately 60 l min^{-1}. The 1/8" tubing was 10 cm in length and had an ID of 0.03". This information will be added to the methods section.

RC: 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.

AR: The transmission curve was calculated in two stages using two approaches. For the compounds in the lower *m/z* range, transmission coefficients were calculated using the approach of Taipale et al., 2008, utilising the compounds contained in our on-site gas standard. For the higher *m/z* range, where no suitable compound was present in our standard, the classical transmission approach of Steinbacher et al., 2004 was adopted using a range of liquid standards. These standards included the higher *m/z* compounds xylene (*m/z* 107) and camphor (*m/z* 153) and the resulting transmission response was compared with the former approach to yield empirical sensitivities for the higher *m/z's*. As monoterpenes were present within our gas standard we were able to derive direct sensitivities for the sum of *m/z* 81 and *m/z* 137. The sum of the two *m/zs* was used in order to compensate for the effects of humidity and fluctuations in drift tube parameters which can affect the relative proportion between the two *m/z* fragments (Tani et al., 2004).

Calculating transmission coefficients empirically undoubtedly increases the level of uncertainty of vmrs, but this level varies depending upon the approach adopted. The approach of Taipale et al. (2008) is thought to lead to vmrs with an associated uncertainty of ± 30% (e.g. Misztal et al., 2010), whereas vmrs calculated using the Steinbacher approach can vary by as much as ±100%. With this in mind, empirically derived vmrs for the lower *m/z* range, e.g. acetic acid and MVK+MACR,have a lower level of uncertainty than those in the higher *m/z* range e.g. *m/z* 83 (Hexanals) and *m/z* 85 (EVK). The remaining compounds presented in this study were all contained within our gas mixture and therefore sensitivities were calculated directly and the uncertainty much lower.

In our revised manuscript we will include this additional information.

RC: 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?

AR: The lagtime analysis was done automatically using a program in LabVIEW. This program searched for the maximum in the cross correlation within a 25 s time window. This will be clarified in the revised manuscript.

RC: 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.

AR: We thank the reviewer for pointing out our oversight. We have revised the calculation for 0.5 s which gives an estimate of high frequency flux loss of typically < 2%. The manuscript has been updated to include this.

We are also aware that further high frequency damping can occur due to the long sampling line which is why we chose to compare the PTR-MS LE fluxes with those measured by an open path IRGA. This has helped to give us an estimate on the potential flux losses that might be expected and as the analysis shows this should not exceed 30%.

RC: 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.

AR: We accept that this analysis needs further explanation. This section will now read:

"In contrast, the low frequency flux losses, arising from insufficient averaging periods, were more significant, as shown by Fig. 1. The *y* axes in this figure show sensible heat fluxes calculated using averaging periods of increasing length, from 1 hour (panel A) to 2.5 hours (panel D) during the OP3 campaign. The *x* axes show the same data but the averaging periods are compiled of individual 30 minute data files knitted together. A high pass filter was applied to each 30 minute file which ensured fluctuations from eddies with a time period greater than 30 minutes could not contribute to the flux measurement (Moncrieff, 2004). The slope of the regression between the two sets of fluxes provides an estimate of the flux lost due to the use of a 30 minute averaging period. The results show that eddies with a time period of between 30 and 90 min increase the flux of sensible heat (*H*) by 15%, while eddies with a period of 150 min carried a further 6% of the flux."

RC: 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.

AR: The reviewer is correct. We will remove this statement in the revised manuscript.

RC: 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?

AR: We have considered the chemical losses of isoprene in detail in a manuscript currently under preparation. We will include the following brief statement and new figure in the revised manuscript:

"The high measurement location of 75 m atop a hill introduces the potential for flux divergence for the more reactive compounds such as isoprene, caused by changes in both convective mixing and isoprene chemistry across the day. We therefore estimated the effect of both isoprene chemistry and transport on the measurements made at our site.

In order to approximate the time taken between isoprene emission and detection by our measurement system, we estimated boundary layer mixing times using the convective velocity timescale (τ_{mix}), calculated as a function of time of day.

$$\tau_{mix} = \frac{z}{w_*}$$

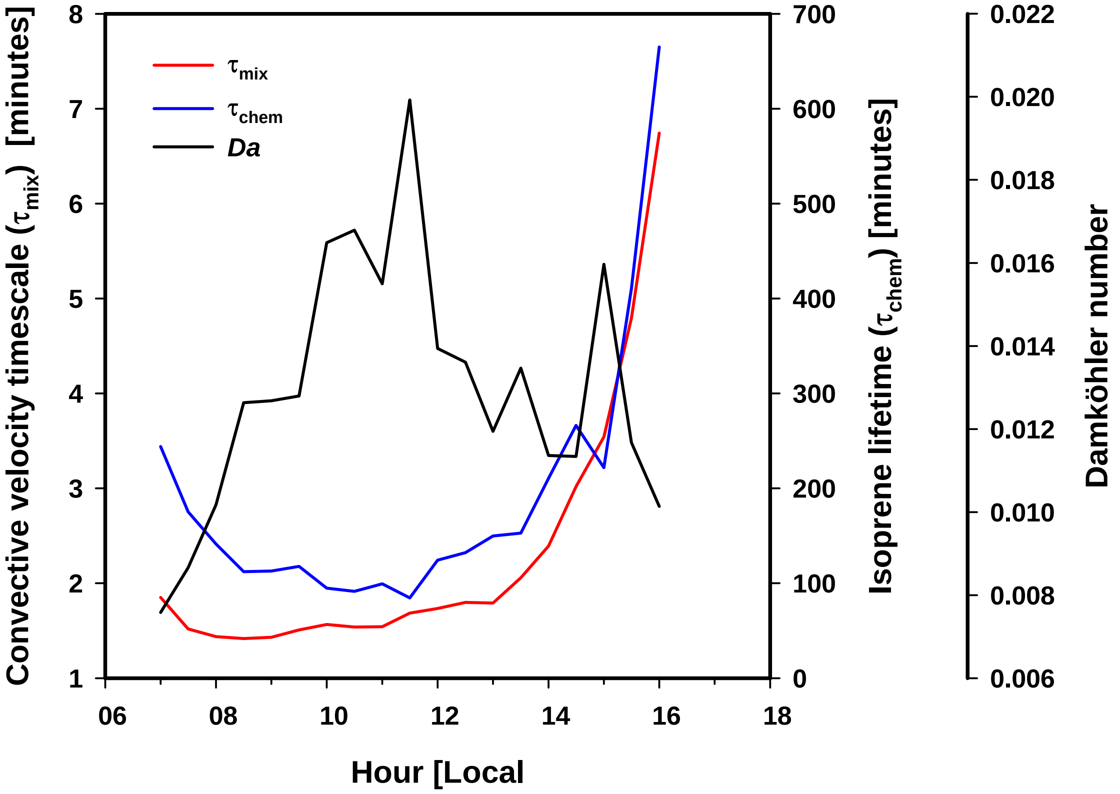
Where *z* is the measurement height which was between 100 and 125 m above the average canopy top, here we use an arbitrary value of 125 m and w_* is equal to

$$w_* = \left[\frac{g \times z_i}{T_v} F_H \right]^{1/3}$$

where, *g* is acceleration due to gravity (9.81 m s^{-1}), T_v is potential temperature, and F_H is the kinematic heat flux. The isoprene lifetime (τ_{chem}) was calculated using the isoprene + OH rate coefficient as a function of the ambient temperature (measured at 30 m) and the OH concentration which was directly measured at a height of 5 m at the base of the GAW tower (Whalley et al., 2010). Figure 4 shows τ_{chem} (blue line) and τ_{mix} (red line) which follow a similar pattern, with shorter mixing times and isoprene lifetimes occurring in the late morning and increasing steadily throughout the afternoon. The net effect of these two processes on our measurements of isoprene was calculated using the Damköhler number (black line),

$$Da = \frac{\tau_{mix}}{\tau_{chem}}$$

A *Da* number of 1 or greater would indicate reaction times to exceed transport times resulting in a total loss of isoprene. Figure 4 shows the *Da* number to follow a distinct diurnal pattern, with the largest isoprene losses occurring throughout the late morning and indicating a maximum 2% loss of isoprene. It should be noted that this calculation only considers the chemical loss after the compounds exit the canopy top and further chemical processing is likely to occur before emissions escape the canopy.



(New) Fig 4. The average boundary layer convective mixing velocity timescale (τ_{mix}) and isoprene lifetime (τ_{chem}) for the period 02 - 21 July 2008 above a tropical rainforest. The Damköhler number (black line) indicates the amount of isoprene that would be lost to chemical reaction before detection by our measurement system, which was located at 100 – 150 m above the forest canopy top. Because the GAW tower is located on a hill it is not possible to give a more precise measurement height.

RC: 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?

AR: Variations (standard deviations) on the *m/z* 33 channel were generally high but of a fairly constant amplitude. Consequently the detection limit for methanol was relatively high despite the high sensitivity for this compound obtained in the calibrations. However, there were no patterns in the background signal on *m/z* 33.

RC: 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.

AR: A new figure will be added.

RC: 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.

AR: We will revise this sentence as follows: “As the isoprene emissions are transported away from the canopy they react to form more MVK+MACR which gradually accumulates in the boundary layer and thus the ratio increases steadily throughout the day. . .”

RC: 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.

AR: The reviewer is correct. It is largely assumed that there are very few temperature-dependent plant emitters in the tropics as tropical plant species tend to lack the specialist structures required for monoterpene storage. Nonetheless, previous leaf-level measurements conducted in Borneo have observed temperature-dependent emissions of monoterpenes from some dipterocarp trees (*Dryanobalanops lanceolata*) (personal comms. Owen, 2010). In this instance the emissions were thought to be a consequence of mechanical damage (e.g. herbivory) to the cuticular wax. Emissions from damaged plants can be considerable and obviously the amount of monoterpene volatilised will be dependent upon the ambient temperature.

As our flux footprint was dominated by dipterocarps, temperature-dependent monoterpene emissions could not be ruled out prior to our measurements. It was only by using a combination of flux measurements and co-located in-canopy concentration profiles that we could conclude that temperature-dependent emissions were not important at this site.

We will add a statement in the revised manuscript mentioning the previous findings of Owen (2010) and the potential for temperature dependent emissions due to herbivory and plant damage.

RC: 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 negligible (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.

AR: There is no contradiction here, but we concede that our explanation could have been clearer. In section 3.2.1 we discuss early morning emissions trapped in the still shallow nocturnal boundary layer and their subsequent venting as that layer breaks up later in the morning. These emissions are driven by the early morning light and temperature, which occurs before the boundary layer breaks up and typically occurred on those mornings where there was little or no cloud cover. If the canopy was emitting compounds at night we would observe the venting every day which is not the case. In the revised manuscript we will try to make a clear distinction between early morning emissions and nocturnal emissions.

The data shown in Fig 6 will be reduced to 10 days which will make the features discussed in the text easier to discern.

RC: 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.

AR: We would argue that because we are fitting the G06 algorithm to our directly measured fluxes the effect of light attenuation through the canopy has been fully captured by our measurements. Therefore the functional form we present is in fact representative of the canopy-scale response to PAR measured at the top of canopy.

RC: 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.

AR: It appears that there is some misunderstanding of what we have written. Our statement: "Model estimates using the *standard coefficients* compare reasonably well with measured values, confirming temperature and light to be the primary drivers of observed emissions" refers to the *standard coefficients* (i.e the Guenther et al., 2006 response) which, as shown by figure 6 are not light saturated during the daytime.

RC: 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.

AR: We agree that it is difficult to make out some of the detail in figure 6 and therefore we will reduce the amount of data shown to 10 days (see response to earlier comment).

We will delete the last sentence "this is not unexpected…"

RC: 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 different from zero?

All of the fluxes shown in this paper had first passed a rigorous set of quality checks. One of these checks involved calculating the precision of each flux measurement. This test involved ensuring that the peak in the cross correlation function exceeded a given threshold (in this case 2 x the standard deviation of the CC at +140 to +180 s and -180 s to -140 s from the true lag time). This value is shown as error bars on the isoprene and monoterpene fluxes shown in figures 4A and 4B, but was also applied to all of the measured VOCs. The application of this quality check enabled us to identify and reject fluxes that fell below our limit of detection and hence were not statistically different from zero. As highlighted in the figure caption, the greyed bands shown in Fig 7 indicate the standard deviation of the average half hourly fluxes. As the plots shown in this figure are of average fluxes taken over an extended measurement period they may be very close to or zero, but the individual measurements that make up that average were all statistically different from zero.

RC: 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 monoterpenes 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).

AR: We appreciate the reviewers point, but feel a discussion of the biology of monoterpene emissions would go beyond the scope of the current manuscript.

Technical comments

RC: Page 11978, line 10: ". . .alsobenchmark. . ." should be ". . .also benchmark. . ."

AR: This was changed.

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

AR: Figures were re-labelled.

RC: 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.

AR: The revised manuscript now uses 2 significant figures only.

RC: 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.

AR: We thank the reviewer for drawing our attention to this manuscript which gives details of measurements made at the Tapajos site subsequent to those reported by Rinne et al. (2002) which we already list in table 3. We will include the results from this paper into a revised Table 3.

RC: Figure 1 has insufficient caption. It is hard to understand the message of the figure.

AR: The figure caption will be expanded and more explanation will be given in the text (see our response above).

RC: 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.

Markers will be added.

RC: Figures 4 a and b have too much data to be informative. One cannot see the shapes of diurnal fluxes.

AR: We disagree with the reviewer on this point. We feel it is important to show the flux time series in relation to the meteorological drivers. The diurnal profiles of these compounds are shown in Figure 8 of the discussion paper.

RC: The message of Figure 6 could be better conveyed with model vs measurement plots.

AR: We agree that correlation plots would be useful, but still feel it is important to show the time series which demonstrates features discussed in the text. We will therefore add two further panels to this figure showing the correlation between model and measurements.

References:

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