

We would like to thank reviewer 2 for their very useful comments on our manuscript and suggestions for its improvement. We have replied to each point in turn below.

## General Comments

**RC:** My most serious concern is that the dataset collected during the field campaign has been too finely parsed with the goal of producing independent papers. There are numerous citations to other manuscripts that are not yet available (in press), and the value of this dataset has been diminished. I feel the authors have left a lot on the table with the goal of producing additional publications. In particular, there should be better synthesis of the VOC gradient data and the GC results. This point is relevant to the leaf-level data also. It's difficult to review the totality of this research contribution with so many in-press references.

**AR:** The reviewer raises two interesting points here which we think deserve some further discussion.

When completed, special journal issues can be a fantastic resource for researchers. They are particularly useful for conveying the findings of consortium projects such as OP3 and ACES, which involve a focused set of complementary but independent measurements and modelling efforts. In addition, special issues in EGU journals have the added bonus of allowing students and fixed term contract researchers such as myself to submit work to meet their own deadlines rather than having to wait for other colleagues and collaborators to complete papers. The ultimate success of a special issue however, hinges on the level of cohesion achieved between manuscripts, which is something we have worked hard to achieve within the OP3/ACES special issue in ACP. As the reviewer points out, this creates problems for reviewers who do not have access to the unpublished manuscripts. We fully acknowledge that within our manuscript there are numerous references to as yet unpublished work. However, cross referencing between papers is what gives the finished special issue cohesion. We would strongly deny that we have “left material on the table” with a goal to future publications. The current manuscript contains all our flux data from this site with a very complete analysis of it. Hopefully our reasoning for not including additional data will become clear in our individual responses below. In many cases, the requested data, for example, the in-canopy gradients or the leaf level measurements, tell their own story which deserves publication in their own right.

As reviewer #3 pointed out in their comments, references to unpublished work must not only cite, but also summarise, all the findings that are relevant to the current manuscript. With this in mind we have reviewed our references to unpublished work and ensured that a sufficient summary has been given in each instance (the specific details of these changes are listed below).

**RC:** A secondary issue is that more details of methodology should be included. This is emphasized in individual comments below. Because of the complexity of combining PTR-MS and eddy covariance in the tropics, it is essential that all these details are included. In particular, see the comment about the additive errors (page 11984).

**AR:** The reviewer makes a valid point here which was echoed in comments made by Reviewer 1. In response to reviewer 1 we have already added more details to the method section and where appropriate we have made further changes in direct response to the issues you raise below.

## Specific Comments

**RC:** 11976:22-25 Although these are both valid points, the inference is a bit off. I would not describe BVOC fluxes as a fraction of NEP. Ecosystems that are net carbon sources can also emit BVOCs. The accounting mentioned in the abstract (0.4% of assimilated carbon) is more relevant.

**AR:** The reviewer is correct, we have reworded this sentence as follows “Trees assimilate carbon from the atmosphere through the process of photosynthesis, as a result of which tropical forests are estimated to sequester 1.3 Pg of carbon per year (Lewis et al., 2009). Some of the assimilated carbon...”

**RC:** 11977:14 Adding “In the presence of nitrogen oxides” before “Finally” might help readers that are unfamiliar with this concept.

**AR:** We will make the suggested change.

**RC:** 11977:23 The following reference includes data from flux measurements in the Amazon basin: Müller, J.-F., T. Stavrakou, S. Wallens, I. De Smedt, M. Van Roozendael, M.J. Potosnak, J. Rinne, B. Munger, A. Goldstein and A.B. Guenther. 2008. Global isoprene emissions estimated using MEGAN, ECMWF analyses and a detailed canopy environment model. *Atmospheric Chemistry and Physics*, 8: 1329–1341.

**AR:** Reviewer 1 also pointed out this paper, which we will make reference to in our revised manuscript.

**RC:** 11978:7 Again, Muller et al discusses this seasonality issue, backed up by some data.

**AR:** We will include a reference to Müller in this section.

**RC:** 11978:10 separate alsobenchmark

**AR:** done.

**RC:** 11979:1 Should just be degrees, not degrees C in lat/long.

**AR:** Well spotted...I think this was down to me using “find and replace” when converting the manuscript to Latex. This will be changed.

**RC:** 11979:17 “north east” to “northeast”

**AR:** This will be changed.

**RC:** 11979:20 Give the flow rate and length of the 1/2 inch tubing.

**AR:** These details will be added – please see our response to reviewer 1 for details.

**RC:** 11981:6 Since the standard with multiple compounds was available during OP3-III, you could compare the measured sensitivities to the Taipale technique and see if you were justified by its application during OP3-I.

**AR:** While this is a good idea in theory, Taipale et al. (2008) show that the measured sensitivities can vary substantially due to changes in the abundance of the primary ion count. This effect can be countered somewhat by using the normalised primary ion count and normalised sensitivities, but variation can still be present as a result of changes to the transmission (mainly due to the ageing of the SEM detector) and fluctuations in the humidity of the air sampled (Taipale et al., 2008). With these considerations in mind, a comparison with measured sensitivities from OP3-III, which themselves were quite variable, probably cannot provide a clear “justification” for the sensitivities chosen during OP3-I.

**RC:** 11981:22 I think 2 degrees C is incorrect here. Maybe 200? Maybe a PDF issue?

**AR:** Well spotted...this should read 200 C and will be changed in the revised paper.

**RC:** 11981:22–4 There is no discussion of potential atomic mass interferences. For example, furan, a product of biomass burning, has the same molecular weight as isoprene. The manuscript alludes to a GC, but only states briefly its use for compound identification. Here is a specific point where incorporation of another dataset is necessary for publication.

**AR:** Two GCs were taken to Borneo for the OP3 project. One GC-MS was operated by Lancaster and a GC-FID was operated by the University of York. Unfortunately the GC-MS which we had intended to use for compound identification had experienced a major fault on arrival which could not be repaired in the field. The GC-FID was located at the base of the GAW tower and sampled at a height of 5 m. The GC-FID was used to target specific compounds, namely isoprene, acetone, acetaldehyde, methanol and the suite of monoterpenes, but it did not target the potential interferences such as furan at  $m/z$  69 and propanal at  $m/z$  59. Therefore these measurements cannot help with compound identification. Equally a comparison of isoprene concentrations measured by the PTR-MS and GC-FID tell us little, as the 70 m separation between sensors means they are measuring at different ranges, from, as shown by the plots in Fig 5, a very heterogeneous source of VOC emissions. This issue is discussed further in the paper recently published in this special issue by Pugh et al (2010). Therefore, unfortunately, we do not have GC-FID or GC-MS data that can help unambiguously resolve the identity of our PTR-MS  $m/z$  69 or  $m/z$  59. However, Table 1 of our manuscript already lists the potential compounds detected at each  $m/z$ , but we acknowledge that some discussion of these potential  $m/z$  interferences is warranted. We have added a short paragraph describing these in the revised manuscript.

RC: 11981:24 Since line 22 has “summary,” replace “summarized” in this sentence (or vice versa).

**AR: This has been changed.**

RC: 11981:25 – 11982:1 First, what did you use for your scalar concentration ( $X'$ )? Was this procedure repeated for every mass? It should always be the same lag for every mass, correct? Unless some compounds were sticky in the tube? Next, I assume you lagged the cross-correlation function over the 25 seconds? I don't think that's clear. Finally, you need to be careful when doing a lag and max procedure (if that is what you did). If there is no flux (for example, isoprene at night), you will calculate a small positive flux since you're picking the max point. The procedure works great during the day when there are strong fluxes, and perhaps the quality assessment is accomplishing this same goal. If so, be explicit about that.

**AR: In response to similar comments made by reviewer 1 we have added more information about our lag time analysis. As the quadrupole has to scan each  $m/z$  sequentially the lag time is not the same for each  $m/z$ . We therefore apply the lag analysis for each individual mass of every 25 minute averaging period. This obviously takes a long time, but it is worth doing to improve the accuracy of our measurements. The lag time can also vary slightly due to the efficiency of the pump and also with the ambient air temperature and pressure. As the reviewer points out, adsorption or condensation in the lines could also affect the lag time, especially for the more polar compounds. A maximum in the cross correlation is searched for across a 25 s time window. As the reviewer points out, during the daytime this procedure is highly effective and for compounds like isoprene which have a large flux, the peak is easy to identify. However at night time when turbulence is low or if an emission rate is small, determining the maximum in the cross correlation can be problematic. This is why we implement the procedure described by Spirig et al., (2005). Here we take the standard deviation of the cross correlation at distances far from the true (or assumed location) lag time e.g.  $\pm 140 - 180$  s. We then multiply this value by 3 to give the measurement precision at the 99.7% confidence interval. We then use this value as a proxy for the limit of detection of our system, rejecting any peak that does not exceed this value.**

RC: 11982:17 The 90% rate is after the application of the  $u^*$  filter described in the preceding paragraph, correct? If so, make clear? How much data were rejected by that filter? Please state.

**AR: Yes, the  $u^*$  filter was applied first. For the period of our measurements  $u^*$  fell below our chosen threshold of  $0.15 \text{ m s}^{-1}$  for approximately 27 % of the time. It should be noted that the flux data that passed our other quality checks i.e data were above the limit of detection etc are were plotted in Figures 4A and 4B as greyed out data. We have added a statement to this effect in our revised manuscript.**

RC: 11982:22 Move the left parenthesis to just before “Helfter.”

**AR: this was changed.**

RC: 11982:27 – 11983:6 Can you give a reason/speculate why this site is influenced by such low-frequency eddies?

**AR: As the mean eddy size scales with height we would speculate that the influence of low frequency eddies is solely a consequence of our very high measurement location (75 m on the tower, plus the height of the hill upon which it is located gives an average value of between 100 and 150 m above the canopy top in the valley. Interestingly the estimated flux loss of between 15 – 20% is very similar to an analysis of sensible heat data obtained on the comparably high telecom tower in central London (see Langford et al., 2010).**

**We have added a sentence summarising the above.**

RC: 11984:8 You first estimate that you might be losing 15–20% due to a measurement time that was too short (11983:6), and you then lose “<30%” due to condensation. These losses should be additive, correct? I don't want to be too critical, since you are being very thorough in your error analysis. But please address this point. Also, shouldn't the relatively low pressure in the sampling line reduce the effect of condensation?

**AR: Yes, we believe these errors should be additive and we have made this clear in the revised manuscript.**

RC: 11985:12 Give the details on your isoprene lifetime calculation. 40 minutes seems short, but maybe OH concentrations were assumed to be high? Is this number from Karl et al 2004?

**AR: Following a comment from Reviewer 1 we undertook a detailed analysis of the chemical losses of isoprene. From this analysis we were able to make a much more accurate estimate of the isoprene lifetime by using**

measured OH (from a height of 5 m) and adjusting the rate coefficient for the ambient air temperature. This showed the average isoprene lifetime to in fact be approx 100 minutes at midday. We have amended this section of the paper to fit with these new findings.

RC: 11985:29 – 11986:2 Issue of splitting the publication of the GC results. This is another case where it is necessary to include at least enough GC results to confirm the mass identifications.

AR: We refer the reviewer to our previous response to the GC measurements.

RC: 11986:17 Should be Figures 4a and 4b. Maybe more clear to make two separate figures? Your call.

AR: We have chosen to keep the figures as 4a and 4b.

RC: 11987: 12 Another instance where the dataset has been parsed very finely. The issue of the fluxes from the boundary layer breakup is interesting, and you have the information necessary (gradient data) to explore this further.

AR: We agree with the reviewer on this point. Inclusion of the gradient data could strengthen this section. However, the two days when this effect was most noticeable were the 9<sup>th</sup> and 11<sup>th</sup> of July. Unfortunately, due to the great difficulties associated with operating a PTR-MS within a tropical forest canopy, the VOC gradient system was only operational between 12<sup>th</sup> – 19<sup>th</sup> July and therefore can add little to this discussion.

Following advice from reviewer 3, where we have cited the currently unpublished gradient work we have now given a more comprehensive summary of these data.

“As part of the OP3-III field campaign, Ryder et al. (2010) utilised a second PTR-MS and automated winch system to measure vertical profiles (1 – 32 m) of VOC mixing ratios within the forest canopy. The targeted compounds included isoprene and monoterpenes and their source/sink distributions were derived using inverse Lagrangian modelling. These data did not show build up of either isoprene or monoterpenes inside the canopy during the night and that dark emissions were negligible (Ryder et al., 2010).

RC: 11988:14 “under storey” to “understorey”

AR: This was changed.

RC: 11988:16 “rates” to “ratios”

AR: Done.

RC: 11988:29 – 11989:8 Another instance where the dataset has been parsed very finely. Here, a significant amount of material is alluded to, and the paper has not appeared on APCD yet. Much of the value of this paper is the discrepancy between the measurements and MEGAN. The leaf-level data are an important piece of information, and the details are not available to assess their merits.

AR: The data we refer to (Owen et al, 2010) were collected by another group and are not our property. They will be separately published in the special issue. We have however endeavoured to include a more detailed summary of the leaf-level measurements and their findings in response to comments made by reviewer #3.

“During the period between OP3-I and OP3-III Owen et al. (2010) made leaf-level measurements of isoprene and monoterpene emissions from the 25 most dominant over- and understory tree species located within the flux footprint of the GAW tower. These were sampled in situ and in triplicate using 3 controlled environment leaf cuvettes which were set to 30 °C and a PAR value of either 500 or 1000  $\mu\text{mol m}^{-2} \text{s}^{-1}$ , depending on whether the leaves were shaded or sunlit. The inflowing air was scrubbed to remove pre-existing VOCs whereas the CO<sub>2</sub> and humidity were allowed to follow the ambient conditions. The out flowing air was sampled onto tubes packed with Tenax and Carbotrap and were stored at 4 °C until analysis by GC-MS could take place in the U.K. These measurements contributed to a larger database of SE Asian forest emission rates compiled between 2000 and 2008, based on field-work in and around the Danum Valley area in 2000 and 2004, and from Dipterocarp rainforest species growing in the Yunnan Province, China, in 2003 and 2005. The database emission factors were used with vegetation survey data for different sample plots in the forest around the GAW tower for biomass weighted emission extrapolations for the plots. Thus best bottom-up estimates of canopy emissions were obtained for different sample plots with values ranging from 0.9 to 2.3  $\text{mg m}^{-2} \text{h}^{-1}$  for isoprene and from 0.2 to 1.0  $\text{mg m}^{-2} \text{h}^{-1}$  for total monoterpenes (Owen et al, 2010), which were in agreement with our direct canopy-scale flux measurements.”

RC: 11989:9 Add Muller et al to the results in Table 3.

**AR: This was done (see our response to reviewer 1).**

**RC: 11990:8** Why was Tmax further constrained? Probably a good idea, but explicitly state the reason.

**AR:  $T_{max}$  was further constrained in order to keep the temperature response within environmentally realistic bounds. A  $\pm 50\%$  freedom would obviously be too high. In our revised manuscript we have included our reasoning for this lower constraint.**

**RC: 11990:9–10** Did Owen gather temp & light curves from enclosure measurements? This would be a very interesting comparison.

**AR: We agree that this comparison would be very interesting and well worth including, but regrettably light and temperature curves were only obtained from leaf level measurements made at the Sabahmas Oil palm plantation and not during the rainforest measurements.**

**RC: 11990:20–21** There are two Hewitt et al., 2010a's and no 2010b. I assume this refers to the second one. Again, it's difficult to assess this paper with so many references to manuscripts in preparation.

**AR: Yes, the reviewer is correct here. This reference is to "Hewitt et al., Circadian control reduces isoprene emissions from forests and moderates ground-level ozone". This has been changed to 2010b in the revised paper.**

**RC: 11990:26** Because the x-axis contains the entire dataset (for phase III), it's difficult to detect these interesting discrepancies. I see the high values early on the Jul 9, but not on Jul 10.

**AR: Figure 6 actually only shows 20 days of data from phase III, but as you and indeed reviewer 1 point out it is difficult to make out the detail. In our response to reviewer 1 we suggested we reduce the number of days shown to 10 and include two further panels showing scatter plots of model vs measurements. This makes the details easier to pick out the features discussed in the text. We should also point out that the peaks occur on the 9<sup>th</sup> and 11<sup>th</sup>, not the 10<sup>th</sup> as stated in the original manuscript. We will circle these events in the revised figure.**

**RC: 11990:23 – 11991:11** While I agree with your reasoning here, you've alluded to other explanations which might explain some of the discrepancy. This reduces the clarity of your current discussion and makes the paragraph moot. Would the hypothetical variations in BER explain this discrepancy? Also, did Owen collect any leaf-level data that shed light on this issue? The current paper seems a bit of a teaser, and the rest of the story will come later.

**AR: The measurements made by Owen et al. were made in the period between OP3-I and OP3-III and therefore cannot shed light on the observed temporal trends. The discrepancies between measurements and model cannot be fully explained by using variable BER. We have added a sentence to the revised manuscript explaining this.**

**RC: 11991:19–20** Be explicit about why this is "not unexpected" for MTs. Isoprene is also light dependent.

**AR: This sentence was removed. Please see our response to reviewer 1.**

**RC: 11991:24–26** Although a subtropical forest, it would be interesting to contrast your results to: Lerda M, Keller M. 1997. Controls on isoprene emission from trees in a subtropical dry forest. *Plant, Cell & Environment* 20: 569–578.

**AR: We thank the reviewer for drawing our attention to this manuscript which shows temperature and light response curves for a number of sub tropical species. Contrasting these findings with our own would be a welcome addition to the manuscript and we have done so in our revised paper.**

**RC: 11992:1–11** This is very important, but worthy of more discussion since it's a major conclusion of your paper. While I completely agree that more measurements are necessary, you should explore why your results are so different from the MEGAN value. Could inter-annual variability be responsible? You briefly mention seasonality in the Introduction, and you should return to that point here.

**AR: The base emission rate is a tree species specific parameter and there is no reason to expect a forest on one continent, with one tree species distribution to have the same or similar BER to another forest on another continent, with a completely different tree species distribution. Inter-annual variability may well be partially**

**responsible, but there is no evidence to suggest that 2008 was abnormal at this site. Seasonality is very limited at this equatorial location. We have therefore not amended the text in response to this.**

**RC:** 11993:10 Another reference to unpublished work. I'm not sure the flux data alone is sufficient to support the conclusion of this paragraph. I understand you hedge your bet with "suggests," but this is not enough. Also, you find a small net deposition, but is this significant? Because of non-linearities and potential flux loss associated with condensation, could the actual flux be positive? Make the paragraph more cautionary, and address the significance issue.

**AR:** This sentence has been revised to say "Canopy profile measurements of methanol mixing ratios made by Ryder et al., (2010) showed elevated values close to the forest floor and their inverse Lagrangian modelling of the vertical source/sink distributions indicates the forest floor to act as a source for methanol at certain times. Previous studies have shown methanol to be emitted during the decomposition of leaf material (Fall, 2003). However, our canopy-scale flux measurements showed periods of both emission and deposition, with small net deposition. Previous studies in Amazonia have also shown both positive and negative fluxes of methanol, but the net exchange has always been reported as positive (Karl et al., 2004). suggest that photo-oxidation is its primary source and results from the CiTTyCAT chemistry box model indicate a methanol formation rate above the forest canopy of  $1.7 \times 10^5$  molecules  $\text{cm}^{-3} \text{s}^{-1}$ , equivalent to about 0.6 ppbv  $\text{day}^{-1}$ ."

**We are confident that the net deposition flux is significant. Even if a flux measurement suffers from very high flux losses it is not possible for the sign of the flux to change. As we point out to reviewer 1, although these fluxes are small, in order for them to register as a flux they must pass a rigorous set of quality checks (please see our response to reviewer 1 for details) and therefore they are significantly different from zero**

**RC:** 11993:26 Another reference to unpublished work. In this case, this point isn't central to the rest of the paper, so you can either add more information or leave for the story for the forthcoming publication.

**AR:** We agree that this sentence is not central to the rest of the paper and have removed it from the revised manuscript.

**RC:** 11994:4–19 Since CO<sub>2</sub> fluxes were only measured during the day and only for a relatively small part of the year, any reference to a "net carbon sink strength" is problematic. I understand what you are saying, but the term usually implies temporal summation.

**AR:** We agree totally with the reviewer and have changed this to "Tropical forests assimilate carbon during the daytime and studies have shown that they currently act as a net carbon sink (Grace and Rayment, 2000). However, the carbon assimilated during the daytime is offset somewhat by the emission of VOCs from both the forest canopy and forest floor."

**RC:** 11995:6 What is the rationale behind the selected NO emission rate? The model results will be very sensitive to this parameter.

**AR:** The rationale for, and the models sensitivity to the selected NO emission rate has been described in detail by Pugh et al., (2010).

**RC:** 11995:4–18 I like the effort to carry your results a bit further with the modeling work. But I do have a couple of concerns. You cast this in terms of net carbon exchange, but it's difficult to get excited about 0.04%. Or even the 0.4% that you start with. Be specific. What is the relevance of this section? Just to say that BVOCs are trivial for carbon accounting? Second, are you accounting for biogenic secondary aerosol formation? Is that part of the dry or wet deposition? Do you assume that anything with a high vapour pressure leads to deposition? You should make this point more clear.

**AR:** Although trivial, the point of this is for completeness of carbon accounting.

**The CiTTyCAT model does not include SOA formation. We will include the following sentence in the revised manuscript to make this point clear. "The model does not include the formation of secondary organic aerosol, however the yields for isoprene are only a few percent (Hallquist et al., 2009)."**

**RC:** 12007: Sesquiterpenes and estragole are listed in the table, but not mentioned elsewhere in the paper.

**AR:** Estragole and sesquiterpenes were amongst the VOCs we targeted during the campaign. However, these compounds were not detected above our limit of detection. We have added a sentence explaining this in the revised manuscript.

**RC:** 12010: DEC is not defined in the Table caption. vDEC is defined in the paper, so just tidy this up.

**AR:** We have added DEC to the table caption and have amended the measurements listed as EC to vDEC to maintain consistency with the rest of the manuscript.

**RC:** 12012: Add a sentence that briefly explains the difference between the x and y axes.

**AR:** Please see our response to reviewer 1 regarding this figure.

**RC:** 12017: Give more explanation on the bottom wind rose. Both normalized and raw fluxes are displayed, correct?

**AR:** Yes, these show both raw and normalised (30 C and 1000  $\mu\text{mol m}^{-2} \text{s}^{-1}$  PAR). We have given a clearer explanation in the revised figure caption.

**RC:** 12018: It's difficult to get a lot of details out of this graph. It would be helpful to display these data as a scatter plot (measured vs. fitted).

**AR:** We agree with the reviewer and have added two further panels showing scatter plots.

**RC:** 12021: Here, you are plotted night time CO<sub>2</sub> data, but in the text you've stated the data are no good. Either remove it or add a cautionary note to the figure.

**AR:** we have added a cautionary note to the figure.