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Comment

Interactive comment on “In situ measurements of isoprene and monoterpenes within a South-East Asian tropical rainforest” by C. E. Jones et al.

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Received and published: 12 May 2011

The authors thank both reviewers for their constructive comments. We address specific comments from anonymous referee #2 below. Please note that all page and line numbers refer to those in the modified manuscript.

Overall: This paper provides measurement data close to ground level of a range of biogenic and (presumed) anthropogenic VOCs using GC-FID analyses, as part of a major research project in south-east Asia. The paper is clearly written, but could usefully make greater reference to the existing publications from this research by other groups, accepting that reference to as yet unpublished data is not straightforward. There is also very little discussion of the role of dynamical mixing on the control of ground-level concentrations, yet the data should be available to include this as an explanatory factor.

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There is also a marked lack of comment on uncertainties, both in measurements (e.g. biases caused by sampling losses) and in interpretations (e.g. spatial heterogeneity around sampling site). Some of the statistical techniques used appear to be non-ideal and should be revisited.

In response to the general comment above relating to the discussion of the uncertainties, we have added the following statement summarising the relevant measurement uncertainties, on Page 5 L114: “The 1σ measurement uncertainties (calculated as the root sum of squares of the measurement precision and all quantifiable experimental uncertainties, such as those associated with flow rates and certified gas standard concentrations) were between 8-13 % for the majority of VOCs, and 11-20 % for the monoterpenes.” Other points are addressed in response to the specific comments below.

Specific comments: Abstract: make reference to “OP3” so that searches of the abstract only will find this keyword

We have amended the following sentence in the abstract to include the project name: “We present observations of isoprene, α -pinene, camphene, Δ -3-carene, γ -terpinene and limonene, as well as oxygenated VOCs (OVOCs) of biogenic origin such as methacrolein, in ambient air above a tropical rainforest in Malaysian Borneo during the Oxidant and Particle Photochemical Processes above a south-east Asian tropical rainforest (OP3) project in 2008.”.

L46: what does ‘in line with’ mean? Quantitative annual emissions, temporal/spatial patterns? Be precise.

Changed this sentence (Page 3 L52) to: “BVOC emissions (by mass) are often dominated by isoprene (Guenther et al., 2000), and estimates of the annual global isoprene flux are comparable with annual global methane emissions (Wildermuth and Fall, 1996; Sharkey and Yeh, 2001).”

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Methods: clearly written but perhaps should be explicit that identification was on basis of retention time. Were analyses made in parallel by GC-MS that would confirm identities of the peaks?

There were no simultaneous GC-MS measurements for these compounds, and identification was on the basis of retention times. Retention times of individual monoterpenes were double-checked during the campaign routinely during the OP3 measurement period. We have added the following sentence for clarification (Page 5 L111): “Individual VOCs were identified on the basis of their GC retention times, which were monitored periodically by analysis of a gas standard (Apel Reimer) and pure liquid injections during the field measurement period.”

L159: somewhere a description of the 4 referenced experiments OP3-I to OP3-III (why not OP3-IV?) is needed. Figure 2 reference doesn't help. I assume from the text that I and III were ground-based, IIII was the aircraft campaign, but it would help to clarify this. 3.1: a comparison is made here with the aircraft campaign, but at least as valuable would be a discussion and comparison with the parallel data from the tower published by Langford et al. in ACP and referred to in passing. Several results from that paper would (a) help with the explanation of some of the variations observed at ground level and (b) pose some questions which need to be addressed. For example, the monoterpene and isoprene flux from the rainforest (measured at the tower) were approximately double in OP-III compared to OP-I, adding to the difficulty in reconciling ground-level concentrations between the two periods. Direct comparisons of average concentrations of methanol, acetone, monoterpenes (sum) and isoprene is possible for top and bottom of the canopy, and some large differences are apparent – why?

There is no “OP3-IV” campaign as the aircraft campaign over Borneo and the second ground based campaign at Bukit Atur took place simultaneously, and so were considered to be part of the same measurement period. For us to label these any other way would be inconsistent with other papers published from the OP3 project. We have amended the explanation of the ground-based measurement periods (Page 4 L91) to

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include explanation of the aircraft campaign schedule: “During OP3-III, aircraft-based regional VOC measurements were made concurrently with the ground-based observations.” We have also amended the Figure 2 caption for clarity: “Time-resolved measurements of isoprene and its oxidation product methacrolein, the monoterpenes α -pinene, camphene, Δ -3-carene, limonene and γ -terpinene, methanol, and selected other VOC thought to be of primarily anthropogenic origin (ethane, acetylene and propane) at the ground-based site at Bukit Atur during April 2008 (OP3-I) and June-July 2008 (OP3-III).”

Regarding comparisons with the Langford et al. data, we can only speculate since the only OH measurements were made from a height of 5 m (co-located with the GC-FID VOC measurements), and there were no OH measurements made at the PTR-MS sampling height of 75 m. As we have stated in the manuscript, the ground-based measurements were subjected to localised pollution in the form of NO during OP3-III, which observations show led to elevated OH mixing ratios compared to the OP3-I campaign. We hypothesise that this meant that the local ground-level measurements of isoprene and other VOCs were suppressed by these elevated OH mixing ratios, while the measurements at 75 m would have been affected by any very localised pollution to a lesser extent, since these observations had a much larger measurement footprint. The mean average acetone mixing ratio reported by Langford et al was 0.7 ppb (range 0.45-0.99 ppb), slightly higher than the acetone mixing ratio based upon the ground level GC-FID measurements reported in this work (mean 0.4 ppb, range 0.2-0.8 ppb), and consistent with increased OH levels at the ground as a result of localised pollution. The mean methanol mixing ratio reported by Langford et al for OP3-III was 1.5 ppb (0.5-2.7 ppb for 5th-95th percentiles), which is actually in relatively good agreement with the GC-FID measurements reported here (mean 1.8 ppb; range 0.9-2.8 ppb). We have included the following sentence to offer some explanation of the differences with the Langford et al data in the manuscript (Page 9 L204): “Levels of isoprene and several other VOCs such as acetone are generally comparable with the lower range of the corresponding mixing ratios reported by Langford et al. (2010), based on their

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measurements from a height of 75 m at the Bukit Atur site during OP3-III. Langford et al. (2010) report an average isoprene mixing ratio of 1.5 ppb, compared to the average of 1.1 ppb isoprene from this work. Since there were no OH measurements co-located with the Langford et al. observations, we can only speculate as to the reason for the differences between the two datasets. However, we feel that the most probable explanation is that the localised pollution and associated elevated OH mixing ratios experienced at ground level suppressed VOC mixing ratios in the local area where our observations were made, whilst the larger sample footprint of the Langford et al. (2010) measurements meant that the impact of local pollution upon VOC mixing ratios was less marked in those observations.”

3.2: there is very little discussion of the dynamical factors that influence ground-level concentrations through controlling vertical mixing, and, as with PAR and temperature, these follow a diurnal pattern. It would be helpful to show a measure of vertical mixing relevant to the measurement height, and its diurnal variation. Essentially, concentrations are determined by the interplay of emissions/deposition, dilution (mixing) and chemical reaction – and all 3 need to be explicitly considered in order to understand the diurnal patterns. The suppression of vertical mixing at night also restricts ‘access’ of BVOCs to reactants (oxidants) and removal of deposited BVOCs (methanol, methylacrolein) to the canopy.

We have now included a plot in Figure 3 to show the average diurnal variation in the wind speed, as an indicator for the extent of vertical mixing. This plot demonstrates that the wind speed was reduced during the morning – mid-afternoon period. The following discussion of the effect of the diurnal variation in wind speed has been included on Page 14 L322: “The wind speed at the site was generally lower between sunrise and mid-afternoon, compared to the late-afternoon - night time period (Figure 3). This suggests that in addition to those environmental factors that directly control emissions (namely PAR and temperature), the wind speed may also impact upon ambient BVOC levels, with reduced wind speeds meaning local emissions were more concentrated in

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the morning and early afternoon, due to reduced mixing and dilution by regional air. We do note, however, that the wind speed was relatively low for the duration of the OP3 measurement campaign at the Bukit Atur GAW station, and the average diurnal variation was only ~ 1.5 m/s.”

L231: why was Spearman’s rank correlation used, rather than other measures? Some explanation is required. Also (see Tables 2 & 3) quoting a correlation coefficient without an indication of the number of data pairs involved is meaningless. Can probabilities be assigned to the degree of correlation? I assume (based on Figure 1) that concentration data were approximately log-normally distributed. If so, statistics such as the geometric mean and standard deviation might be useful additions to Table 1, although the use of percentiles shows the skewed distributions. The 50%ile (median) should be quoted in addition to the arithmetic mean (which will be biased by the skewed distribution).

It is appropriate to use a nonparametric test, such as the Spearman’s rank correlation coefficient, to test correlations between datasets where some values are “off the scale,” that is, too high or too low to measure. Even if the population is Gaussian, it is not possible to analyse such data with a parametric test, since all values are not known (Motulsky, 1995). As certain VOC mixing ratios were below the instrument detection limit in some measurements, we chose to use the spearman’s rank coefficient to test the correlations. Nonparametric tests also generally work well with large samples from Gaussian populations. The P values tend to be slightly too large, but the discrepancy is small. In other words, nonparametric tests are only slightly less powerful than parametric tests with large samples (Motulsky, 1995). We have added the following sentence on Page 12 L272 to clarify this: “The Spearman’s rank correlation coefficient was chosen to express the extent of correlation between VOCs, temperature and PAR since there were data points where some VOC mixing ratios were below the instrument detection limit, and as such it is appropriate to use a non-parametric test for correlation, even when the sample follows a Gaussian distribution (Motulsky, 1995).” Reference: Motulsky, H., Chapter 37 in: Intuitive Biostatistics, ISBN 0-19-508607-4, Oxford University

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Press, 1995.

The number of data pairs used to derive correlations in each case has been added to the footnotes of Table 2 and 3.

The median mixing ratios have now been included in Table 1, and whilst we agree that it would also be nice to also include other statistics such as the standard deviation, we feel that this would result in trying to include too much information in the Table, and that the mean, median and 5th and 95th percentiles describe the data sufficiently.

L236 ff: the discussion here would be helped by reference to the canopy-top data from Langford et al., where the shape of the diurnal cycle is different from that below canopy, and (presumably) reflects the difference in OH reaction and dynamical mixing. Are the explanations offered here consistent with what is observed at canopy-top, where the isoprene concentrations rise more quickly to a peak in the morning, and tail off longer in the afternoon, yet presumably have greater potential loss from reaction with OH?

We cannot speculate on OH levels at 75 m as the only measurements were made at 5 m, co-located with the inlet of our instrument. However, as discussed above, in this case we experienced elevated OH mixing ratios at ground level during OP3-III as a result of localized pollution, and as such we anticipate that OH levels may well have been higher on the ground compared to at 75 m. In light of this, it is difficult to provide any conclusive explanation for the differences in diurnal cycles of isoprene above the canopy and at ground level, and any explanation we could offer would merely be speculation. However, we agree that the difference in the shapes of the isoprene diurnal profiles above the canopy and at ground level is an important point and should be highlighted. Therefore we have included the following sentence on Page 11 L244: “Notably there are some distinct differences between the isoprene diurnal profiles measured at ground level (this work) and at 75 m (Langford et al., 2010), during the same period. Isoprene levels above the canopy appear to increase more rapidly following sunrise compared to the ground level mixing ratios, and decrease more gradually in

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the afternoon, presumably as a result of differences in light levels and mixing rates. However, observations at both heights demonstrate an asymmetric isoprene profile, with maximum mixing ratios in the early afternoon.”

L304: the PTR-MS measures MVK and MACR together at the same mass. Is MVK measureable by GC-FID? If so, how did the sum of MVK+MACR compare with the data reported by Langford et al.? If not, how important is the lack of this information when constructing C budgets (see below)? Some comment on MVK is needed – comparison of methylacrolein data with the MVK+MACR data of Langford suggest an approximately 50% split. The GC method used for this work was optimized for monoterpene observations and was unfortunately not capable of resolving the MVK and ethanol peaks. As such, just as Langford et al. (2010) are only able to report the sum of MVK + MACR, so we are only able to report the sum of MVK + ethanol, and thus we cannot deduce the MVK +MACR signal for a direct comparison with the Langford et al. measurements.

The ethanol + MVK signal correspond to a combined daytime average mixing ratio 3-4 times higher than the MACR mixing ratio, but was originally omitted from Table 1 as we considered that reporting the sum of two species would be of limited interest. However, in retrospect, and in light of the reviewers comments, we have now included the combined ethanol + MVK mixing ratios in Table 1. However, as we are not able to determine individual ethanol and MVK mixing ratios, these VOCs were omitted from the carbon and OH reactivity budget calculations. We do note that it was an oversight not to state this explicitly in the text of the original manuscript, and the following sentence has now been include to make this clear (Page 17 L 377): “In particular, as the GC-FID system deployed in this study was unable to resolve the ethanol and methyl vinyl ketone peaks, these VOCs were not included in the following calculations. Comparison of our methacrolein observations with the combined methacrolein and MVK mixing ratio reported by Langford et al. (2010) suggests approximately equal mixing ratios of MVK and methacrolein.”

3.3 and Figure 7: not all the components (some significant) reported by Langford et

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al. are explicitly included here, e.g. acetaldehyde, acetic acid. Does 'OVOC' include these, or only the compounds listed in Table 1? If data for compounds measured by Langford et al. are available, they should be included in Table 1 and any differences noted in the discussion.

Acetic acid measurements were not made with the GC instrument during OP3. Acetaldehyde was monitored by GC during the ground-based campaign, however instrument difficulties meant that we cannot have total confidence in the values derived from the acetaldehyde peak, and as such we have not reported those mixing ratios here. However, the contribution to OH reactivity was calculated based upon the acetaldehyde values we measured, and although we feel there is a substantial uncertainty associated with these values, we find that acetaldehyde only contributed around 1% of OH removal during daytime and $\sim 2.5\%$ at night. We are not claiming to report an exhaustive list of all VOCs present during OP3, Figure 7 is simply meant to report an interpretation based upon the observations that we were able to make. We have added the following sentence on Page 17 L374 to make this clearer: "It should be noted that the list of VOC species measured by our system (Table 1) is not exhaustive, and contributions from additional VOCs not measured in this work will likely alter the overall contributions of OVOCs, alkenes and alkanes to some extent."

L343: presumably this is "calculated" average daytime reactivity (cf. later) – be explicit
L354: was this reactivity measured or calculated? Be explicit.

The average daytime reactivity we report is indeed the calculated value – apologies if this was not clear. We have amended the sentence on Page 17 L389 for clarification: "The calculated average daytime total VOC carbon concentration during OP3-III was 6150 ngC m⁻³ - approximately double the average night time value (3130 ngC m⁻³)."

We also outline on Page 18 L402 how the OH reactivities were derived: "The reactivity of each VOC with respect to OH was calculated for each instantaneous measured mixing ratio as the product of the VOC concentration (converted from ppt to molec cm⁻³) and the relevant published rate constant, kOH (cm³ molec⁻¹ s⁻¹) (Atkinson et al.,

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1986; Atkinson, 1997; Atkinson and Arey, 2003).”

Table 1: show LOD for each compound and add any additional compounds reported by Langford et al., or comment in text as to why they could not be measured.

LODs have now been added to Table 1. The following footnote has been added to Table 1 to explain the absence of certain VOCs from this dataset: “Note that some VOCs routinely measured by the ground-based instrument, including acetaldehyde and benzene, are not reported as a result of instrumentation difficulties experienced during the OP3 field campaign.”

Tables 2 & 3: see comments above re Spearman’s correlation. What do figures in bold type in Table 3 mean?

Figures in bold type highlight the strongest correlations. A note to this effect has been added to the footnote of Table 3. Also see response regarding Spearman’s rank correlation above.

Figure 1: is the equation based on an orthogonal regression? It should be, as neither measurement is an independent variable.

The equation from the original plot was not based on an orthogonal regression, but Figure 1 has now been updated, and the new plot is based upon orthogonal regression. The changes to the slope and offset were minimal.

Figure 3: add figure showing diurnal variation of vertical mixing (or some surrogate such as wind speed) at the measurement site.

We have included a panel showing the average diurnal variation in wind speed at the site (see discussion above).

Figure 4: show the equations on the plots – they might be of use for future modelling work.

Agreed. Equations have been included in the new version of Figure 4 in the updated

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manuscript.

Figure 5: show equations on (b) as in (a) Equations have now also been included for data in figure 5 (b).

Figure 8: this needs a primary citation, and a little more discussion in text. Presumably the red dots refer to oil palm areas?

The authors do not agree that this figure requires a primary citation, since, although similar plots showing isoprene measured by PTR-MS during OP3 were presented by Hewitt et al., 2010, this data, showing our GC-FID measurements of isoprene during the same campaign, has not been previously published elsewhere. We stated in the text that “the area to the north-east of the Danum Valley conservation area is predominantly oil palm”, however we have amended this as follows, with reference to Figure 8, to make this clearer (Page19 L420): “Strong regional differences were apparent in the isoprene and methacrolein mixing ratios over Borneo. The black open circle in Figure 8 indicates the location of the Danum Valley conservation area; the area to the north-east of Danum Valley is predominantly oil palm, and this area is characterised by regionally higher levels of isoprene and methacrolein, compared to the natural forest (Figure 8) (Misztal et al., 2010).”.

Figure 9: what are the error bars here? Are the mean mixing ratios (as shown) significantly different in a statistical sense? I suspect the wrong metric has been used here, and use of log-transformed data would show the intended message much better. If the uncertainties are as large as portrayed then no conclusions on differences between time of day or source emissions can be drawn, and this section should be omitted from the paper.

This was an oversight on our part for not providing a clear explanation of Figure 9. The data is not presented with error bars to indicate measurement uncertainty – rather the spread of the data represents the range of concentrations measured (5th and 95th percentiles) during the morning and afternoon periods in each region. Particularly

for isoprene and methacrolein, which have strong diurnal variation in their ambient mixing ratios, the mixing ratios measured throughout the course of a morning (6am-12pm) will vary considerably, as will mixing ratios measured through out the afternoon period. So rather than just show the mean values, we felt it appropriate to highlight the range of mixing ratios for each species during each period. However, we do note that there was not sufficient explanation of this in the original manuscript, and have now included the following discussion (Page 19 L426): "Figure 9 highlights differences in the mean morning and afternoon mixing ratios of isoprene, methacrolein and acetylene in air above the natural rainforests of Danum Valley and over the oil palm plantations. Figure 9 also shows the typical range (25th - 75th percentiles) of mixing ratios observed throughout the morning (6am-12noon) and afternoon (12noon-6pm) periods in both locations. The large range in observed isoprene and methacrolein mixing ratios in both regions is a consequence of the substantial diurnal variation in levels of these BVOCs." Note that in hindsight we have also chosen to represent the range of mixing ratios observed throughout the morning and afternoon periods as 25th – 75th percentiles, as this does not detract from the differences in the mean mixing ratios so much as the larger range given by 5th-95th percentiles, which, at first glance we can see might appear to suggest that the mean values just have very large associated uncertainties.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 1189, 2011.

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