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Atmospheric
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Discussions

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

Anonymous Referee #2

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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greater reference to the existing publications from this research by other groups, accepting that reference to as yet unpublished data is not straightforward.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. 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.

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

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

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?

L159: somewhere a description of the 4 referenced experiments OP3-I to OP3-IIII (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?

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.

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).

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?

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.

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

L343: presumably this is "calculated" average daytime reactivity (cf. later) – be explicit

L354: was this reactivity measured or calculated? Be explicit.

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.

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

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

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

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

Figure 5: show equations on (b) as in (a)

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

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.

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