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Interactive comment on “Direct ecosystem fluxes of volatile organic compounds from oil palms in South-East Asia” by P. K. Misztal et al.

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Response to Referee 3

We thank referee 3 for reviewing our article and for his/her very useful suggestions. Our responses are in bold italic text.

General comments

I think this is an excellent project and analysis by some of the leading scientists in this field. I have a few reservations as to the explanation and interpretation of some of the

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data, and the amount of speculation in the manuscript, but recommend publication with minor changes.

Specific comments

1. Instrument issues (methanol and other sensitivity): It is my experience that issues such as the one described for methanol occur as a result of an ageing ion source, which often increases the O₂⁺ signal relative to the H₃O⁺ signal. In general, isotopic O₂⁺ should be the main 'background' for signal at m/z 33, and we have confirmed that for our instrument, except in cases when the ion source became quite old. In those cases, parent ion signal drops steeply within 1-2 weeks. I suggest the authors check into the O₂⁺ signal development before and during the instrument's deployment to this field site, and compare calculated m/z 33 'background' to measured 'background'. Another possibility for low methanol signal is water cluster formation under extremely humid conditions, but the authors generally tried to avoid this situation during deployment using specific instrument settings that I believe should have been sufficient. By the way, I cannot find a clear statement on how 'background' was measured in the field; I assume the same catalytic converter was used that was employed to dilute the gas standards into bags? In this respect: Tedlar bags have been found to affect OVOC mixing ratios (e.g. Schade et al., BGD 2009 and refs therein). That could be a minor issue at high concentrations but then again not considering diffusion out of the bags.

(methanol/O₂⁺) It is possible that the ion source got only very slightly aged as the instrument had been operational at the rainforest continuously for a month before it was transported to the oil palm site. Besides the level of O₂⁺ was very low (<1% and further decreasing throughout the campaign) so ion source must have been in excellent condition. The primary signal was also stable all the time

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without abrupt declines since the quick SEM voltage optimizations were part of the routine in order to keep it at optimal value at all times. As we have replied to a similar comment of the Reviewer 2, the isotopic contribution of ^{17}O ^{16}O $+$ would be less than 1 % of the signal at m/z 33. Therefore the background consisting mostly of O_2H^+ ions and DNOH^+ ions is possible and which is usually the case. The ambient absolute humidity was extreme but indeed the instrument was carefully protected against the high humidity (insulations, heated inlet, reduced pressure in the line, elevated E/N ratio, etc.). These optimizations prevented excessive clustering so the sum of the second cluster (m/z 55) and the main cluster (m/z 37) was typically below 5% of the primary ions. Therefore, it has been concluded that the somewhat higher background for methanol must have been the combination of the extreme conditions and/or the specificity of the instrument.

(catalyst/dilution of the standards) The zero air generator was a custom-built $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst heated to 250 C. There was a reference to the setup in Misztal et al., 2010 but we added the information on the catalyst to SI-3. The 5 min background was scanned every hour by purging the ambient air through the catalyst which worked efficiently for all VOCs including methanol. Its additional advantage was that the exiting VOC-free air was not dry so, as the reviewer suspected, it was used at the site to dilute high concentration standard into clean Tedlar bags using new high quality gas-tight syringes. The diffusion was minimal since the bags were prepared freshly just before the calibration. The calibration range was broad from 20 pptv to 500 ppbv ensuring high precision and minimizing any potential artefacts from using the Tedlar bags. The subsequent calibration in the lab at the same drift conditions but with much less humid air revealed that the high humidity contributed to approximately 20% lower sensitivities in the field.

2. Isoprene oxidation products (section 3.2.3) Oxidation product to isoprene ratios are

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determined by air mass age and OH radical abundance, not measurement height (unless the latter is correlated with OH, meaning very strong vertical OH gradients). The respective half sentence (“despite the large . . .”) should be eliminated.

That is true, but there is also a large vertical gradient of isoprene and MVK mixing ratios, so the difference in heights should be noted. The flux would be expected to be constant with altitude if no divergence is present.

How do you know that MACR+MVK were deposited only to the fronds, as compared to the soil or other surfaces?

We did not state that MVK+MACR cannot be captured by soil, but we know that MACR+MVK can be taken up by plants (Karl et al., 2010) which was evident during those periods when the deposition velocity was significantly less than the maximal deposition velocity derived from R_a and R_b . We added a sentence to mention soil and other surfaces (not just fronds).

Without having read the Langford 2010 paper in detail, I can say with some confidence that chemically produced MACR+MVK fluxes below the sampling level require both decent isoprene emission rates and very high OH radical levels given short transport times on the order of minutes. Were those conditions given at the Malaysian site? The paper indicates that net fluxes were negligible and that isoprene loss was at most 2%. Taking such small loss rates and using the listed isoprene flux data, this should translate into a MACR+MVK flux (yield=55%) of 0.02 mg m⁻² h⁻¹ or less, which I think is close to the flux detection limit and at the low end of measured fluxes in that paper.

The Langford et al. paper reported fluxes of MVK+MACR at ten times the height above canopy used at the oil palm but found no flux divergence for isoprene. The small MVK+MACR flux at the rainforest was statistically determined to be valid owing to the extensive measurement period. Similar questions were

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answered in the discussion of that paper. However, the isoprene production rate was by several factors higher at the oil palm site. OH radical was not measured at oil palm on the ground but was likely to be similarly high over oil palm as at the rainforest (Pugh et al. 2010, Whalley, 2011, Stone et al., 2011). At the measurement height of 3 m above the oil palm canopy the MVK+MACR fluxes were dominated by deposition, and any emission episodes could be regarded as reemission, although a recent report by Bäck et al. (2010) indicates that small quantities of MVK+MACR could be released from root-associated fungi.

So I think the statements on the top of page 12685 are not accurate but rather speculative.

We understand why the sentence may seem speculative to the reviewer but it is very likely true given the large footprint at the rainforest. If MVK+MACR had been measured closer to the rainforest canopy, deposition would have been expected. On the other hand the flux below the detection limit at the rainforest would show much noisier pattern. Nevertheless, we decided to remove this sentence since it is not crucial for the manuscript.

Isoprene and hydroxyacetone, section 3.2.5

Primary HA production from isoprene (as compared to secondary production from MACR) has been explained by Paulot et al., ACP 9, 2009, and that should be cited.4.

This reference was cited.

Toluene (section 3.2.6) It is intriguing to learn of more biogenic toluene emissions found by others. I find this section a bit non-focused though.

Although toluene EC fluxes are novel the focus has been spread on all VOCs.

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The section has been rearranged in the revised manuscript.

Which now is the proposed main source of toluene based on your measurements?

Flowers seem to be the major source.

Is there significant emission from fronds or not.

Only very small emissions were found in fronds possibly due to fungal infestation.

Were flowers present all the time so that toluene was emitted all the time?

Yes, the oil palm gets pollinated all year round although in 5-day cycles which might be different for different flowers/inflorescences/spikelets/trees. It would be interesting to conduct long term measurements at that site and targeted aircraft studies.

I think this section could be better structured and clearer.

This section has now been restructured.

5. methanol, section 3.2.7 It has been previously suggested that methanol is removed from the atmosphere by precipitation but I suggest you consult Schade and Goldstein, GBC 2005, and Crutzen and Lawrence, J. Atmos. Chem. 2000, to convince yourself that this is not a significant sink of atmospheric methanol.

We have added these useful references to the discussion on methanol and modified the section on methanol to reflect reviewer's points. There was a heavy precipitation episode occurring at noon regularly for five consecutive days. These episodes did not seem to affect methanol significantly at oil palm perhaps because the air was already so humid that it was completely saturated with water vapor. Therefore, it seems more likely that methanol was rather

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subject to dry deposition to water droplets and ‘wet’ surfaces, where there is little difference between a rain-wetted and a humid surface other than the volume of water retained in the canopy as a sink for solutes. The precipitation would be more important in dry climates.

Unless some chemical or biological removal process exists in liquid water on the surface (e.g. on leaves), methanol's Henry coefficient is still not large enough to affect its atmospheric concentration significantly. Meaning deposition is rather driven by microbial activity or active consumption by plants, only indirectly affected by moisture as needed for those biological processes. Recent publications suggest that soils are active sinks. Instead of speculating what sources or sinks exist, I suggest to stick to what is evident from the data.

We agree that Henry's law constant cannot explain the whole story, and wet deposition was probably minor, compared to potential dry deposition or removal by bacteria or plants. The latter is an interesting hypothesis, as typically there is a high concentration of bacteria in the soil, waters, and air in tropical regions. Main conclusion is that methanol was deposited at oil palm which was also evident at the rainforest, but we really do not know whether the sink for the downward flux was the leaf surface (wet or otherwise, and presence of epiphytes), the stomata, or the soil. The section on methanol has been restructured and made less specific.

6. acetaldehyde Again, there is speculation about the compound's sources. Suddenly, “anaerobic soil conditions” are mentioned without further explanation. Please elaborate. I do not see the “clearly lognormal distribution” in the supplement. If lower concentrations had been successfully measured, a normal distribution could easily have resulted.

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We cannot see anything wrong in mentioning possible sources for acetaldehyde, which are referred by the reviewer as speculation. One may have multiple sources in these environments and soil may definitely be one of them. There is an evidently lognormal distribution for acetaldehyde (see Fig. S4). A perfectly normal distribution would be extremely atypical in natural systems.

7. Acetone Similar to methanol, the literature on acetone is significantly larger than cited in this manuscript. For instance, the work of Custer and Fall on acetone emission was not consulted/cited, which indirectly explains acetone as a stress/wound compound. I am also wary of the comparison to the Eerdekens model estimates, which are possibly overestimates, and the subsequent speculation about deposition. Due to its long lifetime, acetone fluxes are not strongly correlated with abundances.

We have gratefully acknowledged the work of Custer and Fall in the revised manuscript. It is not possible to make a thorough review on every single VOC unless in a book. We tried not to omit any important reference and the references already take up more than 11 pages of the manuscript. The comparison to Eerdekens model estimates is valuable but the sentence has been restructured not to imply conclusions from this comparison.

8. linear/quadratic/exponential correlations? I think I can quickly create a dataset that has good correlations for ALL of these . . . meaning the qualification of a correlation as being of a particular mathematical relation is arbitrary and should not be used to infer the nature of the relationship. As an example, be reminded that many relationships (e.g. even calibration curves) are clearly not linear although they show correlation coefficients of >0.9 . Using expressions such as “linear correlation” suggests that you do infer the relationship as being linear, which, however, cannot be deducted from the correlation. Consider replacing that wording throughout the manuscript.

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The correlations in environmental datasets may or may not be meaningful. It is true that even if a linear correlation exists one should not infer linear relationships just from the correlation itself without a deeper insight into processes and without knowledge of autocorrelations. Furthermore, most linear correlations cannot be separated statistically from curves of various sorts. The wording has been changed throughout the manuscript to use 'correlation' instead of 'linear correlation'.

9. I find the supplement quite necessary and useful. However, similar care than for the manuscript should be taken to label and explain graphs. Currently, I find some of the graphs poorly labeled. The supplement actually contains a very curious result, namely the light response of isoprene emissions,

The labeling of the supplementary graphs has now been improved.

Figure S7: The authors find the “reverse” of the expected (logarithmic) relationship but did not comment at all. Could this be explained by a horizontal leaf (frond) angle distribution? Or is this simply the result of a T-PAR covariance not accounted for?

The relationship of isoprene emissions as a function of PAR is exponential as expected. When one compares Fig S7 for the response to light with Fig 7b (in the main manuscript) for the response to temperature, it looks that the latter is much steeper. The ‘curious’ result can be explained by the circadian rhythm of oil palms which will be the focus of another paper.

We thank the referee for the interesting comments in this review, and for providing suggestions which led to the improvement of the manuscript.

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