

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

Anonymous Referee #3

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Review of Misztal et al, ACDP 2011

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 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⁺

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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.

2. Isoprene oxidation products (section 3.2.3) Oxidation product to isoprene ratios are 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. How do you know that MACR+MVK were deposited only to the fronds, as compared to the soil or other surfaces? 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. So I think the statements on the top of page 12685 are not accurate but rather speculative.

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3. 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. 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. Which now is the proposed main source of toluene based on your measurements? Is there significant emission from fronds or not. Were flowers present all the time so that toluene was emitted all the time? I think this section could be better structured and clearer.

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. 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.

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.

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 com-

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pound. I am also wary of the comparison to the Eerdeken's 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.

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 deduced from the correlation. Consider replacing that wording throughout the manuscript.

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, 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?

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 12671, 2011.

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