**Atmospheric
Chemistry
and Physics
Discussions**

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 2

We thank referee 2 for reviewing our article and for his/her very useful suggestions. Our responses are in bold italic text.

General comments:

The manuscript 'Direct ecosystem fluxes of volatile organic compounds from oil palms in South-East Asia' presents novel results important for the understanding of the changes in air composition due to oil palm monoculture plantations in the tropical regions. The methods are written extremely well and the use of the Supplements to

give technical data processing details is exemplary, setting the standard to transparency in the data post processing. Too often the data processing is only vaguely mentioned, even though everyone who has done it knows that it is a crucial step in the analysis that affects the results. The authors present in detail the results of the dataset of fluxes and volume mixing ratios of over 10 compounds – a task that is difficult to do in a straightforward and readable way. Nevertheless, the detailed description of the results on each mass will be very useful for the field of atmospheric chemistry and I recommend that this manuscript is published in ACP after minor revisions.

Specific comments

The comments refer to the ACPD numbering. Page 12673: The authors state in the introduction that the flux results are presented in much more detail than it the previous papers published of the campaign data. However, the 2 most overlapping manuscripts have not yet been published. Please mention what the results that are presented here for the first time?

The eddy covariance data of BVOC fluxes above oil palm measured by PTR-MS are presented for the first time in this paper. No earlier toluene emissions from oil palm have been reported either. The papers of Fowler et al., 2011, MacKenzie et al., 2011 and Pyle et al., 2011 are the invited synthesis papers with emphasis on land-use change. These three papers, however, do not report the measurements or modeling results per se but draw on references to other OP3 papers including this one. Since the publishing times are overlapping it was thought to mention these papers in the introduction.

As mentioned before, the methodology is presented in excellent detail, this level of transparency should become a land mark for others to achieve.

We thank you for this kind note.

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3 Results: This part has been rearranged by the authors on the way and has been left as somewhat fragmented and confusing. Please find the energy to revise it so that is it as easy to follow as the first part of the manuscript,

The result section has been reordered to be easier to follow by a reader.

below detailed requests. Titling and grouping of the results is confusing. Section under 3.2 is called 'Fluxes of dominant VOCs' but it is the flux and volume mixing ratio results of each mass, including 3.2.5 on m/z 75 that was not included in the 25 min flux measurement sequence, but VMRs from 5 min scan once an hour. I suggest grouping 3.2.2-3.2.12 under the title 'Characterization of abundant VOCs', that perhaps should have be numbered 3.3?

This suggestion was very useful hence the numbering has been revised accordingly.

I suggest moving combining 3.2.3 'Methyl vinyl ketone (MVK) and methacrolein (MARC) (m/z+ 71)' with 3.4.2 'MVK + MARC deposition'. Please, also move rest of the paragraph from line 25 page 12696 to methods.

This has been done as suggested.

Page 12682, line 15: did the isoprene account for nearly half of the selected or all (selected + scanned) VOCs daytime and one third over the entire period? Please clarify to text.

It now has been clarified in the text that isoprene accounted for nearly half of the mixing ratios of compounds measured in the flux mode plus hydroxyacetone derived from scans (as presented in Table 1). The flux proportions (Table 2) were naturally only for the compounds included in the flux mode. By comparison with the scan in Fig 1a it seems that the targeted compounds constituted the largest VOC portion that can be measured by PTR-MS.

Page 12688, line paragraph Methanol: The authors state that methanol (m/z 33) is

deposited, especially during midday. This may not be the case; instead the deposition at m/z 33 is likely due to a measurement artefact. Methanol and isotope of oxygen give a signal at the same mass 33 Th and their fluxes cannot be distinguished from each other with a quadruple PTR-MS. Read and reference Müller et al, 2010 for a PTR-ToFMS flux analysis on m/z 33.

The reviewer draws attention to an important issue of reliability of methanol measurements by PTR-MS. Because PTR-Tof-MS provides an excellent tool for isobaric mass separation, it was demonstrated that m/z 33 can be impacted by the signal from $O^{17}O^+$ and O_2H^+. The general question is: can previously reported methanol fluxes by PTR-MS be trusted? We strongly believe so, because only methanol will produce a clear covariance whereas oxygen will remain uncorrelated with vertical wind speed. Muller et al, 2010 in fact reported excellent methanol flux agreement between PTR-MS and PTR-ToF-MS. Although the reviewer's argument is interesting, it cannot be applicable for the following reasons: Firstly, any oxygen artifact would affect methanol fluxes only if there was a clear correlation between m/z 32 and m/z 33. Although m/z 32 was not in the MID mode, the 5-min hourly scans of ambient air and catalyst background provided evidence that this was not the case (r^2=0.082). Secondly, m/z 32 was kept low ($<$1% of primary ion counts). ^{17}O isotope is a factor of 2653 less abundant ^{16}O isotope, so its contribution to m/z 33 was less than 1% of the m/z 33 signal. Thirdly, whether O_2H^+ ions or $DNOH^+$ were responsible for the rest of the background at m/z 33, the ambient signals of m/z 33 and m/z 37 were completely uncorrelated (r^2=0.00) (for comparison, the correlation between the signal at m/z 32 and m/z 34 yielded r^2 of 0.87) hence it is not possible that water flux could in any way affect methanol fluxes at the oil palm site despite extreme humidities but at an elevated E/N ratio. In terms of the mixing ratios, the relatively high background measured by purging air through the heated Pt/Al2O3 catalyst was subtracted so should have no effect other than raising the detection limit due to the standard deviation of the noise.

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The amount of oxygen, as well as its' the O18O+ isotope and O2H+, is in turn related to the ion distribution and amount of water vapour in the system. A high water flux can result, in addition to the WPL correctable flux artefact, in an oxygen artefact as well as an artefact flux for any VOC whose signal is humidity dependant. Please read and site Ruuskanen et al., 2011. Elevation in water content leads to lowering of O2+ in the ion source and the reaction chamber and heavy midday transpiration (upward water flux) could lead to an observation of deposition on m/z 33.

As replied above, this would be extremely unlikely to be the case at the plantation. The elevation in ambient water content could not lead to lowering O_2^+ in the ion source but only in the drift tube which would be minor unless in a hypothetical situation in the systems in which the ion distribution would lead to clear correlation between measured m/z 32 and m/z 37. Since the methanol signal was not humidity dependent at oil palm, in the light of Ruuskanen et al., 2011 methanol deposition could not be subject to O2+ artefact. Therefore the answer to the question in the comment title is that m/z 33 deposition flux clearly seems to be due to methanol rather an artifact of water flux dependent O2+ isotope signal loss. Nevertheless the references and a short discussion on this has been added to the revised manuscript (Sect. 3.3.6).

The authors discuss the PTR-MS results based on GC-MS analysis. However, it is not clear if some comparison measurements with GC-MS samples were done during the campaign, or if the comparison is based on literature. An example: Page 12690, lines6-9. Please clarify.

Both. The known contributions to each m/z were identified and an effort was made to look for them in the GC cartridges. There was also a portable GC-MS at the site. However, GC systems also have limitations towards certain compounds such as oxygenated VOCs. In Sect 3.1 we have now added text about GC checks and also refer to the GC section described in Misztal et al.,

2010. The particular example which was brought up by the reviewer refers only to generally known acetaldehyde artefacts which make difficult to achieve the agreement with GC.

3.2.9 Acetone: The authors appear to get confused in comparing concentrations and fluxes of acetone. The footprint of the concentration can be much larger than the flux footprint so it would only be natural that if the oil palm is not the only source of acetone to the air the local concentration does not follow the local emissions.

We do bear in mind the differences in the footprints and clearly the diurnal trend of acetone VMRs (Fig 3d) is broader than the peak in the fluxes (Fig 5). Hence, the oil palm may not be regarded as the only source of acetone. We clarified the sentences which may have been confusing.

Page 12691, lines 19-22: The sentence is confusing; please state what is at odds?

This has been reworded to "The mixing ratio agrees well with the data from the GABRIEL 2005 campaign above the northern Amazonian rainforest but the estimated acetone fluxes of 0.35 mg m-^{2} h-^{1} (Eerdekens et al., 2009) seem to be a factor of 3 larger than in Borneo."

3.2.11 Hexanals: The chapter starts with an intro to why hexanals are emitted and continues with only VMR discussion. Please add discussion on your results.

A short discussion of the small hexanal fluxes has been added to the revised manuscript.

Page 12694, line 13: Please clarify the first two sentences. What is meant by change of default values even with changes in sign?

These sentences were made clearer by explaining how the parameterization of the G06 algorithm using the canopy oil palm data affects default empirical values which are used with MEGAN. It must be noted that these parameters are not suggested to be changed in G06 in the different regions of oil palm

plantation and with the species which are not under circadian control.

Page 12696, line 3: Could the better model fit to oil palm than tropical forest emission also be due to better fit of monoculture of oil palm vs large variety of plant species with different emission potentials of tropical forest?

This is a good point. We think that the canopy studies over monocultures are very helpful for getting their ecosystem response.

I recommend combining the Results and Discussion sections.

This nice suggestion has been implemented.

Section 4.1: Repetition of already discussed results. The differences of oil palm and rainforest are discussed already and will be examined in detail in MacKenzie et al., The atmospheric chemistry of trace gases and particulate matter emitted by different landuses in borneo. invited submission, June 2011.

The repeating points have been removed.

Section 4.2: Move to methods, e.g. under 2.2 or to its own section.

Done

Technical corrections:

Table 2: Consider changing Methanol to Methanol and O2. Change "Acetal-dehyde" to"Acetaldehyde"Table 3: change latter "**" to "***" in the footnote.Figure 5: Why are the average diurnal values sometimes outside the standard deviation? E.g. MVK+MARC positive average flux at in the late afternoon and negative std. Please check the figure.

We accepted all the technical corrections without reservation and applied the corrections. We apologize for the technical error of the graphing software, which was corrected.

We greatly thank the reviewer for the discussion and providing excellent suggestions which improved the manuscript.

Pawel Misztal on behalf of other co-authors

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

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