

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 1 Kolby Jardine

The authors thank Kolby Jardine for reviewing our article and for his very useful suggestions. Please find our responses to specific comments in bold italic text below.

This comprehensive paper Misztal et al. is very exciting as it reports the first ecosystem-scale flux measurements of biogenic volatile organic compounds from OilPalm, a plant that is increasingly used as a global source of biofuel. This is an important step in addressing the environmental impacts of biofuel plantations. I

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strongly recommend this paper for publication in Atmospheric Chemistry and Physics. However, there are a number of specific comments the authors should address.

Specific comments

Abstract: The reported isoprene flux of $30 \text{ mg m}^{-2} \text{ hr}^{-1}$ is extremely large compared with other previous measurements in the tropics of $\sim 1 \text{ mg m}^{-2} \text{ hr}^{-1}$ in Amazonia (Karl et al., 2009), $2.5 \text{ mg m}^{-2} \text{ hr}^{-1}$ in Costa Rica (Karl et al., 2004). A extensive discussion on this point is needed.

Indeed isoprene flux from oil palms is extremely large, exceeding that of rainforest emissions reported in the companion paper of Langford et al. (2010) and that from other tropical regions such as Amazonia and Costa Rica. We added these references to the introduction. However, the value of $30 \text{ mg m}^{-2} \text{ h}^{-1}$ is the maximal mid-day flux rather than the normalized canopy basal emission rate (BER) which is stated later in the abstract to be $7.8 \text{ mg m}^{-2} \text{ h}^{-1}$. In order to better clarify this the phrase “maximal values of” has been added to the sentence: “At midday, net isoprene flux constituted the largest fraction (84%) of all emitted BVOCs measured, reaching maximal values of up to $30 \text{ mg m}^{-2} \text{ h}^{-1}$ over 12 days”. Finally the large values are not a surprise as even larger values have been reported in leaf level studies (e.g. Wilkinson et al., 2006; Owen and Penuelas, 2005; Geron et al., 2006). The importance of such high emission rates is discussed in section 3.4.1.

Abstract: Instead of reporting an emission flux of isoprene and a canopy resistance for MVK+MACR, it would be useful to also report deposition flux for MVK+MACR. That way, you can report the fraction of the carbon emitted as isoprene that is recaptured by the ecosystem.

Deposition flux of MVK+MACR was reported in Sects. 3.2.3 (devoted to MVK and MCAR characterization), 5 (Conclusions) and Table 2. However, we appreciate the reviewer’s suggestion to include the value of deposition flux in

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the abstract, which has been done.

Abstract: "We propose that it is important to include deposition in flux models, especially for secondary oxidation products, in order to improve flux predictions." This has already been proposed. See (Karl et al., 2010).

This sentence has been modified: "Consistently with Karl et al., 2010, we also propose ..."

Introduction: "VOCs play many important roles in atmospheric chemistry, for example serving as sinks for OH radicals, and thus indirectly prolonging the lifetime of pollutants and greenhouse gases in the troposphere." This may not be the case. Rapid OH recycling in a low NO_x atmosphere has now been demonstrated in the tropics (Lelieveld et al., 2008).

As the reviewer points out, OH recycling is only relevant in a low NO_x environment. Our text was a general statement on the role of VOCs, not specific to particular NO_x regimes. The OH recycling mechanisms are certainly intriguing but more field data are needed from different low-NO_x regions as additional in-situ evidence for these recyclings. VOCs from oil palms in the vicinity of polluted cities might be particularly strong sinks for OH.

Introduction: I think a few sentences on the biological function of VOCs from oil palm is needed.

Since the scope of the paper is atmospheric, and we would like to keep the article within its limits, we have just added one sentence to the Introduction on the biological significance of VOC: "Examples of important biological functions identified for VOCs include plant protection against mechanical and anoxic stress (Jardine et al., 2009), oxidative stress (Loreto and Schnitzler, 2010), thermal stress (Behnke et al., 2010), herbivore stress (Laothawornkitkul et al., 2008), attraction of pollinators (Misztal et al., 2010) and mediation in metabolic

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processes (e.g. Peñuelas and Staudt, 2010)."

Introduction: "It has only recently been found that oil palms are very high isoprene emitters. . ." How high and relative to what standard?

Relative to other tropical plants. Please also see our earlier reply to the first abstract comment.

Introduction: What is "frond-level"?

Leaf-level.

Introduction: Do you want to include a summary paragraph of what you actually did?

We have included the following text: "Here we report the first above-canopy eddy-covariance measurements of BVOC fluxes from oil palms, using proton-transfer-reaction mass spectrometry (PTR-MS)" We present details of what we did in the main text and supplementary material.

Site and sampling system: What was the actual flow rate through the line? What was the delay time? Did this change?

The flow in the main line was 35 L/min. Regular spot checks showed this did not change throughout the campaign, although because we were not monitoring the flow continuously small changes (e.g. at night) could have been possible. The details are presented in Sect. 2.1. The theoretical (volumetric) residence time was 7 s but the true lag time was derived by cross-correlation technique separately for each half hour period and compound, and varied from 7 – 12 s depending on the compound and its position in the MID cycle (see details in SI-5 on Flux derivation and validation).

Without heating the tubing exposed to the outside of the instrument trailer, loss of VOCs will occur, especially sesquiterpenes. Why was the tubing only heated on the inside of the instrument trailer?

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We heated the line inside the air-conditioned shed but also insulated the outside segment (approx. 1 m) in order to prevent condensation and this was effective despite extremely high ambient absolute humidity. As we wrote in the chapter devoted to sesquiterpenes (3.3.11) the measurements of these compounds are particularly difficult in high humidity (Kim et al. 2009) so the sesquiterpene data should be regarded as a lower limit.

PTR-MS: Please discuss why the long dwell times were used (500 ms) with a measurement frequency of 0.5 Hz and the consequence to miss the high frequency eddies (10 Hz). What was the total cycle time?

This is a good point. The optimal dwell time is a compromise between resolving all high frequency eddies, and the detection limit. Since it is known that high humidity can lower sensitivities (e.g. Tani 2004) it was decided to increase the dwell time at the cost of performing high frequency correction in the post-processing. As elaborated in earlier PTR-MS studies (e.g. Davison, 2009, Taipale, 2008), it might be better for flux derivation to increase the dwell time in order to lower the detection limit and be well within the response time of our instrument (~ 0.3 s). Subsequent comparison of latent heat fluxes (derived from m/z 37) with 10 Hz data from Li-COR revealed that the high frequency losses were below 9 % (see SI-5 for this comparison), so in other words longer dwell times could not bias the flux by more than 9%. The total cycle time was 7 s. Further details on the flux cycle have been presented in the SI and Misztal et al. 2010.

PTR-MS: Please include the primary ion signal (MHz) and the sensitive (cps/ppbv) for each compound and a description of the calibration technique and how often it was done.

As mentioned in SI-3 the level of the primary ions was kept stable in the range of 6.5 - 7.5 cps. We thought that the detection limits (presented in SI-3) were

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more informative than the actual sensitivities but we have now also added a table of sensitivities (Table S1) to SI-3. We performed one calibration in the field toward the end of the measurement period. In addition we performed several calibrations in the laboratory after the campaign under the same drift-tube conditions. The calibration method and the quality control were thoroughly discussed in SI-2.

PTR-MS: It is not appropriate to use m/z 81 to quantify monoterpenes as many compounds can have this mass as a fragment such as the green leaf volatiles (Fall et al., 1999). Without evidence (eg GC-PTR-MS) that m/z 81 is derived exclusively from monoterpenes, it is therefore necessary to quantify monoterpenes using m/z 137. The analysis should be redone using m/z 137.

Perhaps m/z 81 is not the most appropriate way but m/z 137 could also be biased by contributions from sesquiterpenes, oxygenated terpenes and methyl benzoate. We actually did the analysis also using m/z 137 and the sum of 81 and 137 but we prefer to present the data from the most sensitive channel. The approach of using m/z 81 was chosen because of its lower detection limit and because the agreement between m/z 137 and 81 was good for the data points above the m/z 137 DL, so it should be justifiable to use m/z 81. We would not expect high hexenal emissions since the fluxes of hexanals measured at m/z 83 were very small. Finally, GC data at the site found only small amounts of monoterpenes in the fronds. The small emission at the canopy scale could be from the understory plants and /or floral emissions. However, in acknowledgement of the reviewer's point we have added a cautionary note about potential interferences with hexenals on the m/z 81 channel.

Mixing-ratio distributions, detection limits and statistical summary: Please state what the limits of detection are for the different compounds. Stating that they are very low is not useful.

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The detection limits (LODs) derived by two independent methods are clearly presented in Table 1 of the main manuscript. In addition the LODs are graphically presented in Fig S-4. There is already a reference to the supplement and Table 1 in the main text but we have now also added a separate note on detection limits in the reference to Table 1 to make it easier for the reader.

Diurnal trends of mixing ratios: This section needs to be expanded as in its present form (3 short sentences) it is too short to justify including the large figure 3. Please explain details of the patterns of diurnal concentrations. What influences them? Why do some not have a clear diurnal pattern (but I would expect one from these biogenic compounds).

We accept this section might appear somewhat short. As we would not like to repeat the same information as we included under the section of “Characterization of abundant VOCs”, where these trends (or their lack) are thoroughly explained, we have now decided to remove the “diurnal trends of VMRs”(formerly 3.1.2) and “diurnal trends of fluxes” (formerly 3.2.1) but keep the text within the main sections.

Fluxes of dominant VOCs: Why is a resistance approach used from MVK+MACR when eddy covariance data was collected? How does this resistance approach compare with the eddy covariance results?

The resistances were derived in addition to eddy covariance deposition fluxes (see Sect. 3.2.3, Table 2, and conclusions) with the aim to help future studies referring to these values regardless of the measurement technique. The canopy resistances have been derived from measured deposition velocities so the question about the comparison is not applicable.

Methyl vinyl ketone (MVK) and methacrolein (MACR) ($m/z+ 71$): Why would the ratio of MVK+MAC/ isoprene be lowest during the daytime compared with other times?

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The ratio of MVK+MACR/isoprene was derived only for the daytime. In the morning the ratio gradually declined (isoprene photooxidation < isoprene production rate) until its minimum at 13:00 LT (isoprene photooxidation = isoprene production rate), and then increased steadily (isoprene photooxidation > isoprene production rate) before reaching another equilibrium at about 16:00 LT.

Hydroxyacetone (HA) ($m/z+ 75$): The authors should acknowledge the potential presence of methyl acetate at $m/z 75$.

We have now included Me-acetate as a potential contributor among other biogenic esters.

Toluene ($m/z 93$): Authors should mention that toluene emissions has also been observed from a desert plant (creosotebush) (Jardine et al., 2010). Has toluene not been reported in enclosure studies of oil palm?

We thank the reviewer for this reference on the toluene emissions from creosote bush enclosures, which we now include. As well as from eddy covariance measurements, we also found toluene in flower enclosure experiments but only from the male inflorescences. No toluene emissions from oil palm have been previously reported although toluene was found in floral emissions of other Arecaceae species (see Sect 3.2.6)

Figure 1a: How did the authors identify these VOCs as no effort appears to have been made to acquire GC-MS data.

There was a portable GC at the site, and numerous GC cartridges were taken. This greatly helped in the identification of the compounds although uncertainties in misinterpretation still remain despite the intensive effort to look for all known potential contributions. As unambiguous identification is not always possible, the less certain identification was denoted in grey in Fig. 1.

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The manuscript does mention GC analyses in a number of places (e.g. when discussing toluene. when referring to the paper in preparation of leaf level measurements (Owen et al., 2011), and a GC section of Misztal et al., 2010. As well as the GC section, Figure 2 of that paper presented a partial GC scan of the ambient air near the ground.

Figure 2: 2b is missing it's label. Need to define VMR. Acetaldehyde graph needs rescaling.

These have now been corrected.

Figure 4: Why are there lines connecting some points but not others?

The lines connect only the consecutive points. If there was a gap due to flux rejection then the points were not connected.

Figure 7 and 9: These are very beautiful graphs!

Once again we would like greatly to thank Kolby Jardine for his time to review the paper, providing useful comments, references and all the help in the improvement of this manuscript.

Pawel Misztal in consultation with coauthors

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