

## ***Interactive comment on “Seasonality of isoprenoid emissions from a primary rainforest in central Amazonia” by E. G. Alves et al.***

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Dear Referee.

Please find enclosed the updated manuscript entitled, "Seasonality of isoprenoid emissions from a primary rainforest in central Amazonia", "Manuscript number acp-2015-750", by E. G. Alves et al., for consideration for publication as an original research article within the Atmospheric Chemistry and Physics Discussion, 15, 28867, 2015. Many thanks for the time and effort you put into reviewing our manuscript. Below are our point by point responses to the referee comments and a description of the changes made to the article. Sincerely, Eliane G. Alves (On behalf of all coauthors) National

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Anonymous Referee #2

General Comment and Recommendation: This is a well written study that reports vertical profiles of isoprene, total monoterpene, and total sesquiterpene mixing ratios within and above canopy during the dry, dry-to-wet transition, and wet seasons. The results contained in this report are very useful to the larger community as confirms prior findings such as the seasonality of isoprenoid emissions due to seasonal changes in light, temperature and phenology. Other insights are provided, but overall this study suggests that long-term measurements are needed, especially for improving BVOC model parameterization in forested areas. I strongly support publication in ACP. I only have a few comments for the authors to consider below before full publication is considered:

Referee comment 1: Page 28878, Lines 25-29: Were total sesquiterpene mixing ratios higher during nighttime because you could actually see them due to decreased reactions with OH radicals? Please clarify if part of this is possibly due to lower OH radicals or other oxidants (including NO<sub>3</sub>) during nighttime? In general, do the authors have a sense of radical budgets at this site, either through prior measurements or box modeling estimates?

Reply 1: We do not have measurements of OH radicals and NO<sub>3</sub> for this site. However, because NO<sub>3</sub> is produced by the reaction of NO<sub>2</sub> and O<sub>3</sub>, and because these two compounds have low concentration in Amazonia, we suggest that higher mixing ratios of total sesquiterpenes at night might be also due to the reduction of oxidative reactions during nighttime compared to daytime. We have changed it accordingly in the text. Line 383: Another reason for the higher total sesquiterpene mixing ratios at nighttime might be because of the reduction of oxidative reactions owing to the decrease of OH concentrations in the dark (Goldan et al., 1995) and low concentrations of nitrogen oxides (NO<sub>x</sub>) (Andreae et al., 2002), ozone, and nitrate (NO<sub>3</sub>) in Amazonia (Martin et al., 2010). Referee comment 2: Sampling artifacts by PTR-MS: Can the authors

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comment at all if the isoprene estimates from PTR-MS are influenced by breakdown of multi-functional peroxides at  $m/z$  69? I wonder how much contribution there is to this ion. I know Martin's group has nicely resolved this with ISOPOOH interfering with signals at MACR and MVK. Like the AMS, I do have some newly inspired reservations (from Martin's nice work recently published on this) about our lack understanding of decomposition of oxidized organics in PTR-MS. I think all the authors on this manuscript likely agree this is a concern.

Reply 2: We think that the breakdown of other compounds does not affect significantly the  $m/z$  69. Isoprene oxidation products, especially hydroperoxides produced via the HO<sub>2</sub> pathway, less likely make considerable contribution to  $m/z$  69. One evidence is presented in Figure S8 in the ACP paper (Liu et al., 2013 Supplement). This figure shows the change of  $m/z$  69 (nominal isoprene) and  $m/z$  71 (nominal Methyl Vinyl Ketone (MVK) + methacrolein (MACR)) with the decrease of trap temperature, when sampling air from the chamber for both HO<sub>2</sub>- and NO-dominant conditions. Hydroperoxides were removed by the cold trap, causing the decrease of  $m/z$  71 signal. However, the signal of  $m/z$  69 did not have a significant change, suggesting a negligible contribution of hydroperoxides. Additionally,  $m/z$  71 has been reported as the only dominant product ion of ISOPBOOH and ISOPDOOH standards synthesized by Frank Keutsch group for H<sub>3</sub>O<sup>+</sup> mode (Rivera-Rios et al., 2014). Furthermore, in a site with strong isoprene emitters, other compounds less likely affect the PTR-MS measurements of isoprene (de Gouw et al., 2003). This can be shown in a previous study carried out in the same site of this study, showing that 80% of  $m/z$  69 was isoprene (furan = 20%) (Karl et al., 2007), and in another site near Manaus where measurements with PTR-MS and GC-MS showed good cross-validation for isoprene (slope 1.12) (Yáñez-Serrano et al., 2015). Based on those evidences, we assume  $m/z$  69 is isoprene.

De Gouw, J., Warneke, C., Karl, T., Eerdeken, G., van der Veen, C. and Fall, R.: Sensitivity and specificity of atmospheric trace gas detection by proton-transfer-reaction mass spectrometry, *Int. J. Mass Spectrom.*, 223–224(0), 365–382,

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doi:[http://dx.doi.org/10.1016/S1387-3806\(02\)00926-0](http://dx.doi.org/10.1016/S1387-3806(02)00926-0), 2003.

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Liu, Y. J., Herdlinger-Blatt, I., McKinney, K. a. and Martin, S. T.: Production of methyl vinyl ketone and methacrolein via the hydroperoxyl pathway of isoprene oxidation, *Atmos. Chem. Phys.*, 13, 5715–5730, doi:10.5194/acp-13-5715-2013, 2013.

Rivera-Rios, J. C., Nguyen, T. B., Crounse, J. D., Jud, W., St. Clair, J. M., Mikoviny, T., Gilman, J. B., Lerner, B. M., Kaiser, J. B., De Gouw, J., Wisthaler, a., Hansel, a., Wennberg, P. O., Seinfeld, J. H. and Keutsch, F. N.: Conversion of hydroperoxides to carbonyls in field and laboratory instrumentation: Observational bias in diagnosing pristine versus anthropogenically controlled atmospheric chemistry, *Geophys. Res. Lett.*, 41(23), 8645–8651, doi:10.1002/2014GL061919, 2014.

Yáñez-Serrano, A. M., Nölscher, A. C., Williams, J., Wolff, S., Alves, E., Martins, G. A., Bourtsoukidis, E., Brito, J., Jardine, K., Artaxo, P. and Kesselmeier, J.: Diel and seasonal changes of biogenic volatile organic compounds within and above an Amazonian rainforest, *Atmos. Chem. Phys.*, 15(6), 3359–3378, doi:10.5194/acp-15-3359-2015, 2015.

Referee comment 3: The quality of Figure 1 should be improved. The figure axes are hard to read and actually look blurred on my PDF.

Reply 3: The Figure 1 was redone with the highest resolution provided by the software used for the plots of this manuscript. New version of Figure 1 was uploaded again to ACP.

Referee comment 4: I would also state I had a hard time reading the Tables as well.

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The text appears too small in my version from the website.

Reply 4: The table 1 was redone and uploaded again to ACP.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 28867, 2015.

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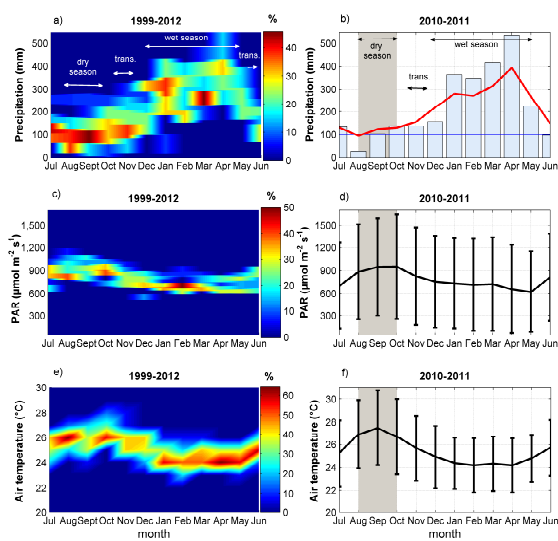


Fig. 1.

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