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Atmospheric Chemistry and Physics
Discussions

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

E. G. Alves et al.

elianegomes.alves@gmail.com

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Dear Referee.

Enclosed please find the updated paper entitled, " Seasonality of isoprenoid emissions from a primary rainforest in central Amazonia", by E. G. Alves et al., for consideration for publication as an original research article within the Atmos. Chem. Phys. Discuss., 15, 28867, 2015. Many thanks for the time and effort you put into reviewing our manuscript which has improved our article. Of particular significance, we now include a new section that present uncertainties related to the inverse Lagrangian Transport flux estimates and to MEGAN estimates. In addition, at the request of the reviewer, we also

include some information about ozone mixing ratios. Another co-author who has contributed to the revision of this manuscript – Dr. Paulo Artaxo (email: artaxo@if.usp.br) – was added. He is a professor at the Institute of Physics of the University of São Paulo, in São Paulo, Brazil. Below are our point by point responses to the reviewer comments and a description of the changes made to the article. The manuscript with revisions (.pdf) is attached to 'Supplement'. Sincerely, Eliane G. Alves (On behalf of all coauthors) National Institute for Amazonian Research (INPA) Manaus, AM, BRA

Anonymous Referee #1

Referee comment 1: Summary "The authors present isoprene, monoterpene, and sesquiterpene profile measurements from central Amazonia during the dry, dry-wet, and wet seasons. They apply a Lagrangian dispersion approach to relate to vertical profiles to sources within the canopy, and interpret the results in the context of predicted fluxes from the MEGAN emission model and inferred fluxes from GOME-2 satellite data. The data shown, and the overall analysis approach, is novel and useful for helping improve our limited understanding of BVOC emissions in this area. My main concern, as discussed below, has to do with drawing conclusions from the model-measurement comparisons without any explicit discussion of the uncertainties contained in either. Most of the figures contain error bars but we're not told what these represent. Lagrangian inverse schemes and BVOC emission parameterizations contain a lot of embedded assumptions and potential errors and the authors need to assess these in a rigorous way before the reader is able to determine to what degree the modelmeasurement differences are meaningful. Once this issue is addressed the paper should be published. There are a few other, more minor, points listed below".

Reply 1: In order to present the uncertainties related to ILT and MEGAN, we have added a section of uncertainties in material and methods. More details are presented below: The main sources of errors for applying the ILT are A correct parameterization of the vertical diffusion coefficient which is based on measured σw/u* profiles. The uncertainty of this factor is the most critical and has been assessed before, based on comparison with Eddy Covariance - it is considered on the order of ±20 %. Because it is a measured quantity it is well constrained though. A parameterization of the Langrangian dispersion time scale (Tl). Changing Tl in the parameterization has comparably small influence. Changing Tl from -20% to +20% will change the integrated canopy flux from -8 to +5%. We estimate the error due to this parameter conservatively as 10%. The entire parameterization (combined effect of 1 and 2) was tested using data from an earlier study (Karl et al., 2009, Karl et al., 2010), where a comparison with eddy covariance measurements was available. Taking the above conservative error assessment the combined uncertainty is ±30%.

Systematic error sources are: Chemical losses: to account for chemistry we used a simple modification of the diffusion coefficient based on Hamba (1993), relying on the fact that the chemical loss will mainly influence the far field of the parameterization. Based on estimated OH and measured O3 densities (Karl et al. 2009, Karl et al., 2010) calculated VOC fluxes were corrected accordingly. Due to low OH and O3 densities in the canopy (<5 x 105 molecules cm-3 for OH and <10 ppbv for O3) the chemical lifetime for isoprene and monoterpenes is considered large compared to the mixing timescale, leading to a chemistry correction on the order of <5% for isoprene and monoterpenes. This systematic error is included, but relies on an estimation of OH for isoprene. The overall uncertainty for isoprene is calculated as 0.3 – 4 % by varying in-canopy OH densities between 5 x 105 and 5 x 106 molecules cm-3. It is noted that an in-canopy OH density of 5 x 106 molecules cm-3 is extremely unrealistic in such a dense canopy and only serves as a very conservative upper limit. Those assumptions were also considered for sesquiterpene flux estimates. However, a sensitive test were carried out to show if the increasing ozone concentrations during the dry season could effectively affect sesquiterpene lifetime and then sesquiterpene flux estimates. For this test, sesquiterpene lifetime was changed in the ILT model using a range from 2 min to 8 hours (upper limit used for isoprene and monoterpene flux estimates). The lower limit (2 min) is based on the lifetime calculated for β-caryophyllene when it is exposed to 24-h average of 7 x 1011 molecules cm-3 of ozone (∼30 ppb) (Atkinson, 2003).

If all sesquiterpenes have similar reactivity with ozone compared to β-caryophyllene, the overall uncertainty for sesquiterpene flux estimates is calculated as up to 20% by varying sesquiterpene lifetime from 8 h to 2 min. It is noted that when considered a lifetime range from 8h to 10 min, the uncertainty for sesquiterpene flux estimates is calculated as up to 4%. The 20 % of uncertainty may be important only during the dry season, when ozone mixing ratios can reach 30 ppbv above canopy (40 m) around noontime.

The number of source layers: If the number of selected source layers is too small, systematic errors of the calculated integrated fluxes arise. We have investigated this effect and found that in the present case, 6 source layers are sufficient to capture >90% of the flux. In the present setup, the ILT model does not converge for more than 9 layers and the numerical solution becomes unstable. If the ILT model would be initiated to only calculate two source layers, the integrated flux would be underestimated significantly (e.g. by up 50%). With 6 source layers we estimate a systematic error of <10% due to this effect. The combined effect of these systematic errors is estimated to be 5-6%.

Summarizing the main sources of errors for applying the ILT and systematic error sources, we added to the manuscript the following paragraphs:

Line 228: “2.4 Uncertainties associated with the ILT and BVOC emission modeling” “The main source of errors for applying the ILT is related to the parameterization of two combined effects: (1) vertical diffusion coefficient which is based on measured σ(w)/u* profiles, and (2) Langrangian dispersion time scale (Tl). Moreover, some uncertainties may be due to systematic error sources with respect to (3) chemical losses, and (4) the number of source layers. The entire parameterization of combined effect (1) and (2) was tested using data from an earlier study (Karl et al., 2009, Karl et al., 2010), where a comparison with eddy covariance measurements was available. Taking the above conservative error assessment, the combined (effect 1 and 2) uncertainty is +/- 30%. To account for chemistry (effect 3) we used a simple modification of the diffusion coefficient based on Hamba (1993), relying on the fact that the chemical loss will mainly influence the far field of the parameterization. Based on estimated OH and measured O3 densities (Karl et al. 2009, Karl et al., 2010) calculated VOC fluxes were corrected accordingly. Due to low OH and O3 densities in the canopy (<5 x 105 molecules cm-3 for OH and <10 ppbv for O3) the chemical lifetime for isoprene and monoterpenes is considered large compared to the mixing timescale, leading to a chemistry correction on the order of <5% for isoprene and monoterpenes. This systematic error is included, but relies on an estimation of OH for isoprene. The overall uncertainty for isoprene is calculated as 0.3 – 4 % by varying in-canopy OH densities between 5 x 105 and 5 x 106 molecules cm-3. It is noted that an in-canopy OH density of 5 x 106 molecules cm-3 is extremely unrealistic in such a dense canopy and only serves as a very conservative upper limit. Those assumptions were also considered for sesquiterpene flux estimates. However, a sensitivity test was carried out to show if the increasing ozone concentrations during the dry season could effectively affect sesquiterpene lifetime and then sesquiterpene flux estimates. For this test, sesquiterpene lifetime was changed in the ILT model using a range from 2 min to 8 hours (upper limit used for isoprene and monoterpene flux estimates). The lower limit (2 min) is based on the lifetime calculated for β-caryophyllene when it is exposed to 24-h average of 7 x 1011 molecules cm-3 of ozone ($\sim$30 ppb) (Atkinson and Arey, 2003). If all sesquiterpenes that occur in this site have similar reactivity with ozone as β-caryophyllene, the overall uncertainty for sesquiterpene flux estimates is calculated as up to 20% by varying sesquiterpene lifetime from 8 h to 2 min. It is noted that when considering a lifetime range from 8h to 10 min, the uncertainty for sesquiterpene flux estimates is calculated as up to 4%. The 20 % of uncertainty may be important only during the dry season, when ozone mixing ratios can eventually reach 30 ppbv above canopy (40 m) around noontime. We have also investigated the effect of (4) - the number of source layers. If the number of selected source layers is too small, systematic errors of the calculated integrated fluxes arise. We have investigated this effect and found that in the present case, 6 source layers are sufficient to capture >90% of the flux. In the present setup, the ILT model does not converge for more than 9 layers and the numerical solution becomes

unstable. If the ILT model would be initiated to only calculate two source layers, the integrated flux would be underestimated significantly (e.g. by up 50%). With 6 source layers we estimate a systematic error of <10% due to this effect. The combined effect of the systematic errors (3) and (4) is estimated to be 5-6%. With respect to uncertainties in model estimates, one of the first quantitative estimates of biogenic VOC emissions (Lamb et al., 1987) included an estimate of uncertainty of 210% based on the propagation of uncertainties in emission factors, emission algorithms, amount of biomass, and land use distributions. This “factor of three” uncertainty has continued to be used as a rough assessment of the uncertainty of biogenic VOC emission model estimates applied on regional scales. A more recent study (Hanna et al., 2005) attempted a comprehensive assessment of each model component and concluded that the 95% confidence range on the calculated uncertainty in isoprene emission was about one order of magnitude while the calculated uncertainty for monoterpenes and other VOC was only ± 20%. Guenther (2013) suggests that the Hanna et al. (2005) study assigns isoprene a higher uncertainty only because more is known about isoprene, and so there are more parameters, and that the lack of observations for quantifying the uncertainties associated with individual model parameters limits the usefulness of this uncertainty estimation approach and instead recommends evaluations that consider the results of model comparisons with canopy scale observations. These studies indicate that models tend to agree with observations within $\sim$30% for canopy scale studies with site specific parameters (Lamb et al., 1996) or for regional scale estimates with known land cover (Misztal et al., 2014) and differ by as much as a factor of two or more for other regional scale studies (Muller et al., 2008; Warneke et al., 2010).”.

Referee comment 2: 28884, 14-22, this section is weak and unconvincing without a robust assessment and discussion of the various uncertainties in both the Lagrangian flux estimates and the MEGAN values.

Reply 2: Relative emissions are emissions normalized to standard conditions of above-canopy PAR of 1500 μmol m-2 s-1 and temperature of 30 °C. Because the highest light and temperature were observed during the dry season, which has a daytime average higher than above- 1500 μmol m-2 s-1 for canopy PAR of and than 30 °C for temperature, it is expected that more relative emissions might be estimated by MEGAN during the dry season, decreasing towards the wet season, since this model is driven primarily by light and temperature. However, when ILT estimates are taken into account, it is observed that isoprene and total monoterpenes presented similar emissions between the dry and the dry-to-wet season and total sesquiterpenes showed maximum emission during the dry-to-wet season. This could suggest that factors other than light and temperature might influence on the seasonality of isoprenoid emissions. The overall uncertainties related to ILT flux was calculated as ± 36% and MEGAN estimates tend to agree with observations within ~30%. However, more observation studies are needed in order to evaluate the degree of observation-modeling agreement, and to improve models.

We have added some more informartion to this sentence:

Line 533: “Relative emissions can be calculated as emissions normalized to standard conditions of above-canopy PAR of 1500 μmol m-2 s-1 and temperature of 30 °C. Based only on light, temperature and LAI variation, relative emissions estimated by MEGAN 2.1 were maximum during the dry season for isoprene, α-pinene, and β-caryophyllene (Fig. 4 c, f, i), when the highest light and temperature were observed. This prediction differs from the ILT flux estimates (Fig. 4 b, e, h), which showed similar emissions between the dry and the dry-to-wet season for isoprene and total monoterpenes and maximum emission during the dry-to-wet season for total sesquiterpenes. The overall uncertainties related to ILT flux was calculated as ± 36% and MEGAN estimates are considered to be in agreement with observations when they are within ~30%. However, more observation studies are needed in order to evaluate the degree of observation-modeling agreement and to improve model approaches, especially for total monoterpenes and total sesquiterpenes, which could present larger uncertainties due to the lack of information about atmospheric concentrations and reactivity of

monoterpene and sesquiterpene chemical species in Amazonia”.

Referee comment 3: 28885, 9-10, similar comment. Clear error analysis is needed to interpret these comparisons.

Reply 3: When Langrangian flux estimates and MEGAN estimates were compared in this sentence, this was a qualitative comparison. In other words, we just attempted to compare the trend of seasonal emissions presented by MEGAN and ILT. MEGAN estimates were driven by light and temperature (measured at the site) and LAI derived by MODIS. MEGAN results showed that when light and temperature were higher, emissions were also higher for all compounds, which was shown in a seasonal trend that suggested decreasing in emissions from dry (September) to wet (January) season. ILT estimates were driven by isoprenoid concentrations measured in the site, and the seasonal trend of emissions presented by this technique showed that, even though that temperature and light were higher during the dry season, some other factors may have influenced emissions locally (e.g. leaf phenology), because similar emissions of isoprene and total monoterpenes were observed between dry and dry-to-wet transition seasons and the highest emissions for total sesquiterpenes were observed in the dry-to-wet transition season. Major quantitative differences between ILT and MEGAN estimates can be shown for isoprene in September, when ILT estimates represent only 4 % of the MEGAN estimates; for total monoterpenes in December, when ILT estimates represented 14 % of the MEGAN estimates; and for total sesquiterpenes in November, when ILT estimates showed emissions two of one factor higher than MEGAN estimates.

We have added more information to the following sentence:

Line 562: “Predictions from MEGAN 2.1 again differed from measured emissions (Fig. 5 b, c, d), showing a reduction in emissions from September 2010 to January 2011. Major quantitative differences between ILT and MEGAN estimates can be shown for isoprene in September, when ILT estimates represented only 4 % of the MEGAN estimates; for total monoterpenes in December, when ILT estimates accounted for 14

% of the MEGAN estimates; and for total sesquiterpenes in November, when ILT estimates were 232% of the MEGAN estimates". These differences may be related to local effects, especially leaf phenology and changes in the atmospheric oxidative capacity over the seasons".

Referee comment 4: 28878, 18-20. Need to state what the error bars represent - it appears visually that this sub-canopy peak is not statistically significant.

Reply 4: Error bars represent one standard deviation. This sentence was removed from the manuscript, because this sub-canopy peak is not in fact statistically significant compared to the profile. Then, the following sentence was added:

Line 366: "As with isoprene, higher mixing ratios of total monoterpenes were observed during daytime, indicating that they are light-dependent, which agrees with the evidence of recent photosynthetic origin of monoterpenes (Jardine et al., 2015; Loreto et al., 1996)".

Referee comment 5: 28878, 24, same comment for sesquiterpene profiles.

Reply 5: Error bars represent one standard deviation. Total sesquiterpene mixing ratios near the ground and at the sub-canopy are higher than mixing ratios above canopy, and this is statiscally significant with 5% of significance level. The significance level "P<0.05" was added to this sentece at line 372.

Referee comment 6: More detail needed on the Lagrangian modeling. Does this include any chemical or deposition terms? It's also not clear how the time dimension comes into play. I presume the concentration measurements are not being related to emissions only in that particular time step but also to emissions in preceding time steps? Such details need to be clarified.

Reply 6: To obtain emissions we use an inverse model approach (ILT), which has been developed by Raupach (see Raupach, 1989). It is termed Lagrangian, because the diffusion coefficient is combined with a Lagrangian time scale of mixing (Tl) within and

above the canopy. Another important piece of information needed is the diffusion coefficient which was determined from measured vertical profiles of σw/u*. Based on this information the model calculates a dispersion matrix (eq 1), which relates a concentration gradient to a source-sink distribution. The two parameters needed to constrain the model (Tl and σw/u* profiles) were based on measurements (σw/u*) and a direct comparison with eddy covariance fluxes during an earlier study (Karl et al., 2009; Karl et al., 2010). This allowed to constrain the ILT for the present study, where measured u* was the main driving factor determining the vertical diffusion coefficient. Since the ILT is applied under the steady state assumption, there is no time dimension necessary, since concentration profiles are used as constraint to infer steady state fluxes for each time step. This approach will yield fluxes for each time step which can be positive (emission) or negative (deposition). To account for chemistry we used a simple modification of the diffusion coefficient based on Hamba (1993), relying on the fact that the chemical loss will mainly influence the far field (diffusive component) of the parameterization. Based on estimated OH and measured O3 densities calculated VOC fluxes were corrected accordingly. Due to low OH and O3 densities in the canopy (<5e5 molecules cm-3 for OH and <10 ppbv for O3) the chemical lifetime for isoprene and monoterpenes is considered large compared to the mixing timescale, leading to a chemistry correction on the order of <5% for isoprene and monoterpenes. This systematic error is included, but relies on an estimation of OH for isoprene. The overall uncertainty for isoprene is calculated as 0.3 – 4 % by varying in-canopy OH densities between 5e5 and 5e6 molecules cm-3. It is noted that an in-canopy OH density of 5e6 molecules cm-3 is extremely unrealistic in such a dense canopy and only serves as a very conservative upper limit. All of these details are now in the section of Material and Methods.

Referee comment 7: Section 2.2, It's fine to refer to other cited papers for method details, but we need some basic information here: how calibration, blanks, humidity dependence were quantified and accounted for. Also, overall uncertainties and LODs for the compounds examined.

Reply 7: We have added the following paragraph into the section 2.2:

Line 155: “Calibration slope (m, ppbv/normalized counts per second (PTR-MS signal)) for isoprene, total monoterpenes, and total sesquiterpenes were obtained twice in the field using the dynamic solution injection technique (Jardine et al., 2010). Solutions of isoprene, α-pinene, and β-caryophyllene standards (> 95% purity, Merk) in 100 mL of cyclohexane were injected into the mixing vial at 0.5, 1.0, 2.0, and 3.0 μL min-1 (30 min each flow rate) with a constant dilution flow of 1.0 slpm ultra high purity nitrogen passing through. The linearity of calibrations was significant, being r2 of 0.92-0.97 for isoprene, r2 of 0.98-0.99 for α-pinene, and r2 of 0.90-098 for β-caryophyllene. Sample air isoprenoid mixing ratios were calculated by multiplying the calibration slope by normalized counts per second (PTR-MS signal) (average of two calibration slopes). Calibration slopes obtained on October 2010 were within 10 % relative to those from the calibration carried out in September 2010 (isoprene 7.2 %, α-pinene – 8.2%, and β-caryophyllene – 2.5%). For 4-7 days before each isoprenoid profile measurement period, ultra high purity nitrogen was run into the inlet of the PTR-MS for 2 h in order to obtain the background signals. The limit of detection for isoprene was 0.14 ppbv, 0.15 ppbv for total monoterpenes and 0.1 ppbv for total sesquiterpenes”.

Referee comment 8: 28877, 15-19, note that GOME-2 passes overhead at âĹij9:30am and does not directly give information related to 24-h integrated emissions. A model is needed to relate the morning measurements to a 24-h average.

Reply 8: It is of course true that the derivation of top-down emissions relies on models - i.e. on both an emission model and an atmospheric model - this is precisely how inverse modelling works. Note that the early morning overpass time does not imply that GOME-2 informs us only about isoprene emissions at this overpass time – not only isoprene and formaldehyde have chemical lifetimes of several hours, but the production of formaldehyde from isoprene involves intermediates (e.g. PAN, MACR, organic hydroperoxides, etc.) of variable lifetimes, as discussed e.g. by Marais et al. (2014). The top-down emission estimate is therefore dependent on the modelled diurnal shape of

the isoprene emission and on the chemical and physical processes affecting isoprene and its degradation products. We have added the following sentence to the manuscript:

Line 336: "Note that given the early morning (9:30) overpass time of the GOME-2 measurement, and the mostly delayed production of formaldehyde from isoprene oxidation, the top-down emission estimate is dependent on the ability of MEGAN to simulate the diurnal shape of isoprene emission and on the parameterization of chemical and physical processes affecting isoprene and its degradation products in IMAGESv2."

Referee comment 9: 28878, 4-16. The inverted vertical gradient at night implies that the isoprene lifetime is shorter near the ground than aloft. Is Nox sufficiently low that NO3 loss would be negligible?

Reply 9: We do not have measurements of NOx concentrations for the site of this study, but based on some measurements of NOx from the Southern Amazonia (Andreae et al., 2002) and on ozone concentrations measured at this site, we assume that NOx concentrations could be also low for this site, which may increase isoprene lifetime at night compared to the daytime. We have added some more information to the following sentence:

Line 361: “In addition, isoprene lifetime increases during nighttime owing to the decrease of OH (hydroxyl radical) concentrations in the dark (Goldan et al., 1995) in light of the low concentrations of nitrogen oxides (NOx) in Amazonia (< 3 ppb above the canopy during nighttime in the dry-to-wet transition season) (Andreae et al., 2002)”.

Referee comment 10: 28879, 8: sesquiterpene ozonlysis: what are ozone levels and what is the corresponding sesquiterpene lifetime?

Reply 10: We have added the following sentence to the manuscript:

Line 386: “With daytime ozone mixing ratios up to 40 ppbv (40 m) during the dry season, sesquiterpene lifetime with respect to ozonolysis above the canopy (40 m) can be 2 min during the daytime and 5 min during the nighttime (Jardine et al., 2011)”.

Referee comment 11: 28881, 13-21: is there reason to think this area could have anomalously low emissions compared to the rest of Amazonia? You refer to the canopy openness and the density composition of isoprene emitters, how do these characteristics compare in this area to elsewhere?

Reply 11: About canopy openness, the main different thing of this site is the fact that there is a dirt road near the tower. So, this may cause some impacts on the canopy density compared to other more remoted areas, where one might see a canopy less opened. With respect to the density composition of isoprene emitters, we speculate that this site has perhaps low fraction of isoprene emitting species. We don't have much information about which tree species are isoprene emitters or not in Amazonia. The main information that we have comes from Harley et al. (2004) study, which showed that from 125 tree species, screened in some different sites in Amazonia, just $\sim$ 38 % of them is isoprene emitter. Moreover, some species are strong emitters and some are weak emitters, and we don't know how strong, weak and non-emitters are distributed in Amazonia. More research is needed to better understand those things. We have added some more information to the following sentence:

Line 450: " However, this could be due to the particular location of the site of this study, such as the relatively open canopy, caused by the proximity to a dirt road, and perhaps the site has a relatively low fraction of isoprene emitting species. Isoprene fluxes measured previously at the same tower site during the wet season were similar (Karl et al., 2009)".

Referee comment 12: 28883, 10-15, since you have ozone data, it seems odd to resort to hand-waving when discussing sesquiterpene chemical losses. Couldn't a quantitative estimate (or at least a range) for this be easily derived, given some reasonable assumption for species composition?

Reply 12: Quantitative estimate of the sesquiterpene losses by ozone is given in the previous sentence: " line 496, ... during the daytime many sesquiterpenes (46%–61%

by mass) are rapidly oxidized by ozone as they undergo withinâĂŘcanopy ozonolysis...". But we have added some more information to the following sentence:

Line 499: "Considering that higher insolation and also higher ozone concentrations were observed during the dry season (ozone daily average of $\sim$ 23 ppbv and $\sim$ 10 ppbv at 40 m in the dry and wet seasons, respectively), an important fraction of the sesquiterpenes emitted by vegetation could be rapidly oxidized by ozone, leading to significantly lower mixing ratios of total sesquiterpene during the dry season (Jardine et al., 2011), which creates a need to account for sesquiterpene oxidation within the canopy when calculating emission rates".

Referee comment 13: 28887, 8-12: why do you expect leaf phenology to differ at your site compared to the broader region?

Reply 13: Because there are uncertainties associated to satellite-derived leaf phenology (Jones et al., 2014), which are mainly due to the heterogeneity caused by the huge biodiversity in this ecosystem (Silva et al., 2013). We have added some more information to the following sentence:

Line 617: "As MEGAN 2.1 was driven with local variations in PAR and air temperature, and with regional variations of LAI (satellite observations at 1-kilometer resolution), this regional variation in LAI may not represent the local effect of LAI variation on local emissions, since vegetation in Amazonia is phenologically distinct due to the huge biodiversity of this ecosystem (Silva et al., 2013)"

Referee comment 14: 28869, 4-5: awkward phrasing, "profiles were collected of the vertical profile"

Reply 14: Sentence rephrased:

Line 31: "In this study, vertical profiles of mixing ratios of isoprene, total monoterpenes and total sesquiterpenes, were measured within and above the canopy, in a primary rainforest in central Amazonia...".

Referee comment 15: 28874, 10: “concentration vector for each level”, shouldn’t this be “concentration vector for the 6 levels”

Reply 15: Sentence rephrased:

Line 187: “where C âČŮ is the concentration (g m-3) vector for the 6 levels...”.

Referee comment 16: All figures: need to indicate what the error bars represent.

Reply 16: We have added the following sentence to the figure captions: “Error bars represent one standard deviation”.

Author’s input: We have added some more information to the “Acknowledgements”: Line 713: “This work was performed at the National Institute for Amazon Research and at the State University of Amazonas with funding provided by the CNPq (fellowship provided to E. Alves by the Brazilian government), and financial support for field work was provided by the Philecology Foundation of Fort Worth, Texas, and the National Science Foundation through the AMAZONâĂŘPIRE (Partnerships for International Research and Education) award (0730305) and instrumentation support (CHE 0216226). We also thank Dr. Scott Saleska for supporting this long field campaign. This research was also supported by the Office of Biological and Environmental Research of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231 as part of their Terrestrial Ecosystem Science Program. The authors would like to acknowledge the advice and support from the Large Biosphere-Atmosphere (LBA) as a part of the Green Ocean Amazon (GoAmazon) 2014/5 project in Manaus, Brazil.T. Stavrakou was supported by the GlobEmission project (No 4000104001/11/I-NB) of the European Space Agency”.

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