Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2017-1083-AC1, 2018

Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Biomass burning emissions disturbances on the isoprene oxidation in a tropical forest" *by* Fernando C. Santos et al.

Fernando C. Santos et al.

fer.cav.san@gmail.com

Received and published: 14 May 2018

Dear Referee#1,

Thank you for your criticisms and suggestions to the manuscript. Most of the modifications were made in the manuscript (attached) and below are the comments to the questions made previously.

Referee#1 1) It would greatly enhance the utility and strength of both the methods and main con- clusions - the variation in oxidative capacity of the Amazon boundary layer between pristine, fresh, and aged smoke plume conditions - in this manuscript to include more discussion of potential sources of error and uncertainty, and the spread in the data. In particular, the lack of ranges and error bounds on measurements from this

study and on the [OH] numbers reported in Table 4 makes them difficult to interpret, because it is not clear (a) whether these results hold broadly for all plumes under all conditions, and for the background under all conditions, and (b) what the uncertainty is in the estimates. There are a lot of assumptions & steps to get from what you measure (which itself has ranges and uncertainties) to what you infer, and I think it's slightly misleading and less useful to report single numbers as averages in the three conditions.

Author comment: 1) Following the reviewer's suggestion standard errors were included in the values reported here (including Table 4). Although the Table 4 has been created to compare the measurements and estimated values from this study with the literature, we also recognize that there is a lack of information level between our study and other measurements in Amazon rainforest. We push forward the details about Isoprene, its oxidation products and OH, using the information about altitude level (surface, boundary layer, free troposphere, cloud layer) and the atmospheric condition (background, fresh and aged smoke). Unfortunately, we do not have the same details in the literature as we have in our study.

Referee#1 Figure 8 does a good job breaking this down to show variation in the product:isoprene ratio within and across altitudes under the three conditions, but it would be nice to see that translated to uncertainties in OH, and to see an expansion in the discussion of potential sources of error

Author comment: Yes, we agree with the reviewer. The OH uncertainty and potential sources of error has been included in the last paragraph in the section 3.3. In Figure 8, the distribution density and its average value, together with number of samples considered, give us a good overview of the data. The average values can simplify the comparison process, but the kernel density distribution show how dispersed can be the measurements.

Referee#1 2) Kind of as a continuation of the previous comment, it would also benefit this manuscript to have more discussion of the departure of your results from those of Karl et al. (2007) and other studies, and whether or not those discrepancies are expected from the differences in methods used between the studies. It is surprising that such similar methods can give such vastly differing results, and merits further description of why the estimates in Karl et al. were two orders of magnitude higher. There is a section listing results of some previous studies (L 388 - 408), but it does not delve far into why different studies found such different values and what reasons exist to believe certain numbers in place of others. In particular, the background values reported in this study seem substantially lower than recent studies that used similar organic ratios (e.g. Liu et al. 2016) - how can these be reconciled?

Author comment: (2) As mentioned in the manuscript (section 2.3), we modified the processing time t in the sequential reaction model to represent not only the vertical transport but also the horizontal atmospheric circulation. The differences in the OH calculated through the two versions of sequential reaction model is due to the attempt to improve the transport time along the atmosphere. The background measurements in this study comes from the classification adopted: specific altitude range (below 2,000 m), time of the day (between 11:00 am and 6:00 pm) and CO levels (threshold of 150 ppbv). These criteria can bring to the result different values. Also, the background value should be understood as a representative value. The Amazon rainforest atmosphere has a background CO mixing ratio typically around 100 ppbv. However, the mean CO inflow into the Amazon Basin throughout the SAMBBA period was approximately 140-160 ppbv. An alternative would be the geographic classification of flights in different groups and for each group having a background value, but the insufficient number of flights (n) for some regions, especially the cleaner regions, restricted the use of such method.

Referee#1 3) The use of a single value for the total yield of [MVK + MACR + ISOPOOH]

from isoprene (0.55) and for the rate of [MVK + MACR + ISOPOOH] + OH (6.1e-11 cm3 molec-1 s-1) seems potentially problematic. Under the range of conditions reported in this study, the pathways of isoprene oxidation can differ drastically, from an overwhelming fraction of the isoprene-derived peroxy radicals reacting with NO (giving combined MVK + MACR yields 57%, from the numbers on L 112, and no ISOPOOH) to very low-NO chemistry in which a large fraction isomerizes (forming MVK and MACR in small yields) and the rest reacts with HO2 to form ISOPOOH in very large yields (up to 93%, Liu et al. 2013). Given that the three first-generation products also have very different oxidation rates, as you note in section S2, the rate of product loss can also vary widely depending on the oxidative conditions (particularly the concentrations of NO). For example, the attached figures show the steady-state daytime [ISOPOOH + MVK + MACR] / isoprene ratio, the steady state [ISOPOOH] / [MVK + MACR] ratio, and the steady-state [OH] as a function of [NO] for various isoprene oxidation models (MCM from Jenkin et al. 2015, Caltech from Wennberg et al. 2018, and GEOS-Chem versions 10 and 11), using the box modeling conditions described in Jenkin et al. 2015. The variations with NO are pronounces. These variations in yields and rates could be treated in different ways: you could just incorporate them as uncertainties in the model, in which case, they merit much more discussion in this manuscript; or, you could use the measured NO in the air masses sampled to calculate the assumed fractions of MVK, MACR, and ISOPOOH produced from isoprene, and from that to calculate the bulk oxidation rate of these products, using one of the isoprene oxidation models shown in the attached figures. You could also consider bringing temperature into the equation, since all the oxidation rates (and some of the yields) vary with temperature as well.

Author comment: (3) We agree with the reviewer on the impact of different reaction pathways may have on the OH estimate provide here and have added a discussion accordingly. We find extremely interesting the suggestion of the reviewer, however we feel that such modification fall outside the scope of the current manuscript, which aimed at studying the impact on OH estimates by Karl et al., (2007) equations through a much improved estimate of transport time. We hope in the near future though to exploit the different reactions pathway might have on the OH estimates accordingly.

Referee#1 L 152 - ISOPOOH is not isobaric with MVK and MACR - it's a decomposition interference. If it was only calibrated with MVK and MACR, do you have some estimate of how efficient the decomposition of ISOPOOH –> m/z 71 was?

Author comment: According to Rivera-Rios et al., 2014, the conversion yields of ISOPOOH into MVK and MACR was observed to be greater than 70%, but the decomposition is known to be highly sensitive to instrumental settings such as temperature, contact time and type of surface materials, especially transition metal surfaces (Liu et al., 2013; Nguyen et al., 2014; Rivera-Rios et al., 2014, Liu et al., 2016, Bernhammer et al., 2017).

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(11), 5715–5730, doi:10.5194/acp-13-5715-2013, 2013. Nguyen, T. B., Crounse, J. D., Schwantes, R. H., Teng, A. P., Bates, K. H., Zhang, X., St Clair, J. M., Brune, W. H., Tyndall, G. S., Keutsch, F. N., Seinfeld, J. H. and Wennberg, P. O.: Overview of the Focused Isoprene eXperiment at the California Institute of Technology (FIXCIT): mechanistic chamber studies on the oxidation of biogenic compounds, Atmos. Chem. Phys., 14(24), 13531–13549, doi:10.5194/acp-14-13531-2014, 2014. Rivera-Rios, J. C., Nguyen, T. B., Crounse, J. D., Jud, W., Clair, J. M. S., Mikoviny, T., Gilman, J. B., Lerner, B. M., Kaiser, J. B., 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,, 1–7, doi:10.1002/(ISSN)1944-8007, 2014. Liu, Y., Brito, J., Dorris, M. R., Rivera-Rios, J. C., Seco, R., Bates, K. H., Artaxo, P., Duvoisin, S., Keutsch, F. N., Kim, S., Goldstein, A. H., Guenther, A. B., Manzi, A. O., Souza, R. A. F., Springston, S. R., Watson, T. B., McKinney, K. A. and Martin, S. T.: Isoprene

photochemistry over the Amazon rainforest, Proc. Natl. Acad. Sci. U.S.A., 113(22), 6125–6130, doi:10.1073/pnas.1524136113, 2016. Bernhammer, A.-K., Breitenlechner, M., Keutsch, F. N. and Hansel, A.: Technical note: Conversion of isoprene hydroxy hydroperoxides (ISOPOOHs) on metal environmental simulation chamber walls, Atmos. Chem. Phys., 17(6), 4053–4062, doi:10.5194/acp-17-4053-2017, 2017.

Referee#1 L 315 - here you say the [MVK+MACR+ISOPOOH]/isoprene ratio is low in fresh plumes, which appears to be corroborated in Figure 7, but on L 320- 321 and later you quote high values of the [MVK+MACR+ISOPOOH]/isoprene ratio in fresh plumes, as shown in Figure 8. How do these coincide?

Author comment: We appreciate this question that help us to avoid a mistake in the manuscript. There is not a classification in Figure 7 about fresh or aged plumes. The Figure 7 only presents the plume interception during the flight B732 (10:00 - 11:30 am) and is possible to observe the different altitude interceptions through the biomass burning tracers. For ∼2 hours as a threshold to differentiate fresh to aged plume, the Figure 8 represent well our results.

Referee#1 L 344-345 - how does an increase in photolysis rates increase the [MVK+MACR+ISOPOOH]/isoprene ratio? If it speeds up oxidation in general, it may remove isoprene faster, but if it also increases the photolysis of MVK, MACR, and ISOPOOH (rather than isoprene) it may cause faster removal of the products instead.

Author comment: According to Apel et al., 2002, the high value for kOH is responsible for the majority of the chemical processing of isoprene by OH. As the rate constant of OH with MVK and MACR are lower than isoprene-OH, we expect an increase in the ratio [MVK+MACR+ISOPOOH]/isoprene, especially in polluted environment. The point has been clarified in L.340

Apel, E. C., Riemer, D. D., Hills, A., Baugh, W., Orlando, J., Faloona, I., Tan, D., Brune, W., Lamb, B., Westberg, H., Carroll, M. A., Thornberry, T. and Geron, C. D.: Measurement and interpretation of isoprene fluxes and isoprene, methacrolein, and methyl vinyl ketone mixing ratios at the PROPHET site during the 1998 Intensive, Journal of Geophysical Research: Atmospheres, 107(D3), 7–15, doi:10.1029/2000JD000225, 2002.

Referee#1 L 378 - two orders of magnitude is a lot! The values quoted from here down to L 408 span a wide range, and it is therefore not clear whether saying the "OH concentration values presented in this study agree in order of magnitude with more modeled and observed values previously reported" (L 388-389) is a useful metric. See general comments (1) and (2) above.

Author comment: The average OH mixing ratio in boundary layer and cloud layer were reported in this study (table 4), with the values varying from 0.1 to 7 x 106 molec. cm-3. Most of the studies mentioned don't have a clear distinction in which altitude the values were obtained (boundary layer and cloud layer) and also very important, no distinction in which ambient condition was reported (biogenic environment, fresh or aged smoke plume). The measurement of the OH in the atmosphere still remain controversial as described in the manuscript, even so, the average values reported in table 4 are in the interval of the majority of the references in the manuscript.

Please also note the supplement to this comment:
https://www.atmos-chem-phys-discuss.net/acp-2017-1083/acp-2017-1083-AC1-supplement.zip

---

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2017-1083, 2017.