Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2017-1083-AC3, 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.

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Received and published: 14 May 2018

Referee comment: How big is the identied increase in oxidation capacity really? Please consider possible uncertainties regarding the analytical OH calculation.

Author comment: As we try to express in the manuscript, there is a controversial discussion about the impact on the oxidative capacity in forest sites. Observational studies conducted in pristine rainforests showing low-NO and high isoprene have consistently reported unaccountably high OH levels, e.g. (Whalley et al., 2011). Rohrer et al. (2014) compiled several previous OH observations in environments characterized by large VOC concentrations, such as forested areas, and concluded that it requires a substantial OH recycling mechanism to reconcile the discrepancy between observations and

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model outcomes based on the conventional understanding of isoprene photo-oxidation (Logan et al., 1981). However, a different school of thought considers these discrepancies between model and observation of OH production due to instrument artifacts. Mao et al. (2012) directly demonstrated the magnitude of potential instrument artifacts by adapting a novel background characterization method called a chemical removal technique, a method to measure OH in parallel with the traditional Fluorescence Assay with Gas Expansion (FAGE). The study also illustrated that the application of the chemical removal technique results in agreement between observed and model-calculated diurnal OH variations based on the conventional isoprene photo-oxidation. Our study is based on the premise that different environments, clean and from biomass burning, have an influence on the oxidative capacity. Due this, we used the [MVK+MACR+ISOPOOH]/[Isoprene] ratio and the hydroxyl radical (OH) indirect calculation to assess the oxidative capacity of the Amazon forest atmosphere in the background, fresh and aged smoke plumes.

Whalley, L. K., Edwards, P. M., Furneaux, K. L., Goddard, A., Ingham, T., Evans, M. J., Stone, D., Hopkins, J. R., Jones, C. E., Karunaharan, A., Lee, J. D., Lewis, A. C., Monks, P. S., Moller, S. J. and Heard, D. E.: Quantifying the magnitude of a missing hydroxyl radical source in a tropical rainforest, Atmos. Chem. Phys., 11(14), 7223–7233, doi:10.5194/acp-11-7223-2011, 2011. Rohrer, F., Lu, K., Hofzumahaus, A., Bohn, B., Brauers, T., Chang, C.-C., Fuchs, H., Haeseler, R., Holland, F., Hu, M., Kita, K., Kondo, Y., Li, X., Lou, S., Oebel, A., Shao, M., Zeng, L., Zhu, T., Zhang, Y. and Wahner, A.: Maximum efficiency in the hydroxyl-radical-based self-cleansing of the troposphere, Nature Geosci, 7(8), 559–563, doi:10.1038/NGEO2199, 2014. Logan, J. A., Prather, M. J., Wofsy, S. C. and McElroy, M. B.: Tropospheric chemistry: A global perspective, J. Geophys. Res., 86(C8), 7210–7254, doi:10.1029/JC086iC08p07210, 1981. Mao, J., Ren, X., Zhang, L., Van Duin, D. M., Cohen, R. C., Park, J. H., Goldstein, A. H., Paulot, F., Beaver, M. R., Crounse, J. D., Wennberg, P. O., Digangi, J. P., Henry, S. B., Keutsch, F. N., Park, C., Schade, G. W., Wolfe, G. M., Thornton, J. A. and Brune, W. H.: Insights into hydroxyl measurements and atmospheric oxidation in a California for-

est, Atmos. Chem. Phys., 12(17), 8009–8020, doi:10.5194/acp-12-8009-2012, 2012.

Referee comment: Line 146 ff: How do the authors assure that ISOPOOH does contribute to the measured m/z = 73 at all ? Has there been any test for this ? How is the inlet system designed to allow measurement of this species ?

Author comment: We reported the data at m/z 71 as the sum of 3 isomers. 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 comment: Line 200 ff: Isn't such quasi-analytical approach prone to errors ? How do OH levels calculated by eqn (2) compare to detailed model results ? Can this be compared to establish the validity of eqn (2) ? How uncertain are the OH concentrations calculated ? Is there any chance to compare the analytical results with, say, a 1-D or a box-trajectory model result ?

Author comment: We appreciate your question and we agree that more tests are necessary. We added the standard error in the Table 4 and in Figure 9 the intervals represent the level of confidence (0.95) used. Your question is very important and guided us to insist in the development of the equation. After improvements and suggestions made by the Referees, we expect in the future apply the indirect [OH] calculation in atmospheric models as a diagnostic tool. We are aware that a lot of work must be done, but still believe that is possible to have it such as tool.

Referee comment: Line 363: Maybe I oversee something but what exactly is that 'Sequential reaction approach' ?

Author comment: Sequential reaction approach or simple consecutive reaction scheme model is an expression for the time rate of change in the [MVK+MACR+ ISOPOOH]/[Isoprene] ratio and derived as a function of [OH], the rate coefficients, and the time available for processing. A consecutive reaction scheme, in which isoprene and the reaction products MVK, MACR and ISOPOOH react with OH is shown by equation (2).

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Please also note the supplement to this comment:
https://www.atmos-chem-phys-discuss.net/acp-2017-1083/acp-2017-1083-AC3-supplement.zip

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