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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Isoprene and monoterpene fluxes from Central Amazonian rainforest inferred from tower-based and airborne measurements, and implications on theatmospheric chemistry and the local carbon budget" *by* U. Kuhn et al.

Anonymous Referee #2

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Report on the manuscript:

Isoprene and monoterpene fluxes from Central Amazonian rainforest inferred from tower-based and airborne measurements, and implications on the atmospheric chemistry and the local carbon budget.

by U. Kuhn et al.

The authors report their results from field measurements in and above a pristine Amazonian rain forest. Three aspects are emphasised: (I) Emission fluxes of volatile organic compounds (VOC) in particular those of isoprene, (II) the contribution of VOC emissions to the carbon budget of the ecosystem and (III) hydroxyl radical (OH) concentrations in the convective boundary layer as inferred from concentration gradients in the mixed layer above the canopy. Isoprene and monoterpene fluxes were determined using the methods of relaxed eddy accumulation and surface layer gradients. The results obtained with both methods agreed well for the monoterpene fluxes but not for isoprene. Another method applied to estimate VOC fluxes from large areas was the mixed layer gradient (MGL) method, a method normally applied to determine fluxes for compounds with low reactivity. Reasonable agreement between fluxes from tower based measurements and MLG fluxes could only be obtained after taking into account a substantial chemical loss of the VOCs.

CO2 exchange was compared with VOC emissions. This led to about 1% as the contribution of emitted VOCs to the net ecosystem carbon exchange, but with quite large uncertainties. The contribution of VOC emissions to this carbon budget may be less than 1% and range up to 9%.

Vertical concentration gradients within the well mixed boundary layer were measured for isoprene and its oxidation products MVK and MACR. Concentration ratios were determined for (MVK+MACR)/isoprene. The dependence of these ratios on height were used to estimate OH concentrations. For this purpose it was assumed that mixing in the CBL was similar for all compounds, that deposition and mixing of air masses in the CBL with air masses from the free troposphere as well as horizontal transport have negligible impact on the concentrations of the respective VOCs. The lowest flight height was used as a base and the time for vertical mixing was determined from micrometeorological data. This procedure to estimate OH concentrations resulted in remarkably high values, nearly an order of magnitude higher than suggested before for regions as the Amazon Basin. Another approach which is based on mass balance was used as

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consistency check. Within the uncertainties of these estimates both approaches led to consistent results.

The content of this manuscript is very interesting. The manuscript contains new and important data and it addresses relevant scientific questions within the scope of ACP. Data regarding VOC emission strengths, the contribution of VOC emissions to the carbon budget as well as data regarding the self cleansing capacity of the planetary boundary layer are indeed relevant. The basic concept using product/educt ratios to infer OH concentrations has been applied before. However, the importance of the addressed matter needs many data including those obtained by the application of established basic concepts. Also the methods used to determine VOC fluxes are established. The concomitant uncertainties arising from using these methods are clearly addressed by showing the differences between the results in particular for isoprene. Nevertheless, the conclusions resulting from interpretations of the experimental data seem justified. Obviously, oxidation of isoprene and the other VOCs does not lead to a massive reduction of OH concentrations at conditions typical for the CBL over an Amazon rain forest. This is in contrast to the predictions made by current chemistry models and indeed an important and substantial conclusion.

Overall the presentation is well structured, the text is written in a precise manner and the manuscript is easy to read (some exceptions of minor importance are listed below). I do not see any major error, there are only some minor points. Consideration of these points would improve the manuscript:

As far as I can read from the text the tower based measurements were not conducted simultaneously to the airborne measurements. If so, it is not easy to compare the results obtained from the MGL approach with those obtained from the tower based measurements. There may have been variations of VOC fluxes from day to day. These would not have been detectable and cause the discrepancies between the results. This possibility should be mentioned.

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Adhering rigidly to kinetic laws, equations 8 and 9 are not correct because the yields of MVK and MACR are different for isoprene + OH and isoprene + ozone reactions, respectively. In order to avoid confusion for a reader I suggest to either write both equations exactly or to give both as approximations which include only OH reactions. The latter case would include deleting the reactions of MVK and MACR with ozone since these reactions are slower than those of both compounds with OH (at least during daytime).

The authors should include a short chapter describing the sensitivity of the fit results on the input data. The results from the GC-FID and GC-MS measurements differed by a factor of approximately 2. The fits were conducted using GC-FID data but without really knowing whether these GC-FID data are correct or the GC-MS data. There are some apparent questions that should be answered: Is the mentioned uncertainty of concentration measurements considered in the uncertainty given for OH concentrations? If not, what would be the result of the fits if the concentrations measured with the GC-FID would be multiplied by 0.55 i.e. assuming the GC-MS data to be correct? Would the use of such lower concentrations lead to non significant differences between the estimates from the fits and previous model predictions or are the uncertainties in concentration measurements not propagated linearly since concentration ratios are used for the fits?

To address these questions in a short chapter would allow the reader to better assess the significance of the discrepancies between previous model calculations and the present estimates. This would improve the good manuscript even more.

There are some typing errors and I furthermore suggest some cosmetic changes with the latter just from my personal perception:

Page 650 line 5: the letter “i” is missing

P. 662, lines 15 to 29: The net CO2 uptake of the Amazon Basin is compared to the VOC emission from the global tropical forest. This comparison should be made for

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same area.

P. 666, lines 8 - 10: Sentence “This is different for the airborne data within the CBL, where the chemical production is smaller and the compounds are exposed to atmospheric chemistry for longer time periods.” This sentence is not easy to understand. If compounds are exposed to atmospheric chemistry for longer time periods the chemical production of the products should be higher. This sentence needs rephrasing.

p. 667, line 4/5: Sentence: “These values are very consistent with the relationship of ..” I suggest to delete the word “very”. Data are either consistent or not consistent.

P. 674, lines 7 - 11: The sentence “ In spite of a good representation of the simulated isoprene flux, the SCM model analysis on the absolute mixing ratios of these compounds indicates that a state of-the-art atmospheric chemistry model might simulate appropriate vertical profiles of the (MVK+MACR)/ISO, but for the wrong reasons, i.e. too high mixing ratios of the respective compounds.“ I do not understand this sentence. I believe that it is intended to state that multiplying nominator and denominator of a ratio with a similar factor does not change the number drastically. If so, I suggest to exchange the word “respective” by the word “all”.

The chapter conclusions is more a summary than a conclusion. I suggest to change the heading to “Summary and conclusions”.

Figure 13: Please delete “[ppb]” at the x-axis.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 641, 2007.