

Interactive comment on “Flux estimates of isoprene, methanol and acetone from airborne PTR-MS measurements over the tropical rainforest during the GABRIEL 2005 campaign” by G. Eerdekens et al.

G. Eerdekens et al.

Received and published: 27 April 2009

We are very grateful for the astute comments of the reviewer, we have performed additional laboratory experiments and runs using a better resolved model. We believe we have addressed them all in the revised version.

Major Comments

1) As suggested by the reviewer, the manuscript has been shortened and reorganised. In particular the description of the GC, isoprene chemistry section and model description have been condensed. The manuscript has now been reduced to 53 pages whilst

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



retaining the same content.

II) We respectfully disagree with the reviewer who suggests excluding the SCM model results. The discrepancy between the model, which expresses the best current understanding of the dynamics and chemistry of the rainforest, is precisely the point we wish to bring over. We believe that a paper including a detailed comparison of the state of the art model and measurement is more valuable than one reporting only the measurement values. There are few such comparisons available in the literature to date and as such the research is a first attempt to determine the model uncertainties in representing the physical and chemical processes. For instance, the reduction of the MEGAN flux values by a factor of two was deliberately made to emphasise the large differences between modelled and measured values. This reduction does not imply that the MEGAN fluxes are incorrect as is now made clear in the text (page 10, line 24). The reason to prescribe the modelled fluxes was to obtain the best fit to the measured concentration values in order to diagnose the likely cause for model/measurement disagreement. In the discussion we make it clear that the model's dynamics (vertical transport of water, heat and tracers) and in particular chemistry are most likely the cause for the discrepancy

III) Reviewer 1 states that the mixed layer budget approach, as presented by Karl et al., (2007), and in Eq. (3) of the discussion paper, is a more commonly applied method for determining fluxes. Further detail is requested by the reviewer on which values have been used this equation, these are now given in the text including the time of day used for this flux calculation. In contrast to the study by Karl et al., (2007) who used this method to estimate the OH concentration over the Tropical rainforest (assuming an entrainment term), we have measured all parameters on the right hand side of equation 3 (including OH) and use this to calculate the net flux ($F_s - F_e$). We obtain values for $F_s - F_e$ that range, for the well mixed afternoon conditions, between 16 and 25 mg isoprene $m^{-2}h^{-1}$ (25p-75p) and a median of around 20 mg isoprene $m^{-2}h^{-1}$ for this region. Note, this takes into account the humidity dependence discussed in point IV below.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



Interactive
Comment

We agree with the reviewer that we did not adequately apply the OH measurements in our empirical assessment of the data. In the revised manuscript we now use OH to back-calculate the surface isoprene mixing ratios and compare this derivation to the values obtained from the sum of parent and oxidation products (ISOP+(MACR+MVK)+(MACR+MVK)/39*61) and with the formal mixed box treatment.

IV) Subsequent to the campaign, humidity controlled calibrations were performed in the laboratory. Following the suggestion of reviewer 1 we have applied these derived corrections to the data. We retain the comparison with the GC results but do not apply to correction factor to the PTR-MS data. The corrections for humidity driven sensitivity changes have led to a small decrease in the reported mixing ratios for isoprene (2.7% to 9.1%), MACR+MVK (6.1 %-12.3%), methanol (19.3 % to 28.5%) and acetone (<1%). The resulting orthogonal distance analysis expresses a linear relationship between the PTRMS and the TD-GCMS with a slope of 0.81 and an off-set of 34 pptv ($R^2=0.895$) but does not change the general overestimation of the isoprene mixing ratios by the GCMS over the PTRMS even though the PTRMS is less selective and was very likely detecting other compounds at m/z 69. On this basis we choose now, not to correct the PTR-MS data to the GC-MS data but instead merely make the comparison. As requested by reviewer 1 all cartridge data is now shown on the Figure, and the confidence band has been removed from the Figure for clarity.

Minor comments

The manuscript has been proof read by a native English speaker.

1: We agree with reviewer 1 that the statement 'is consistent with global emissions' is confusing without further explanation and therefore we have removed it from the abstract.

2: We agree with reviewer 1 and remove mention of the compensation point approach from the abstract.

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

3: The reviewer is correct we refer to the entire vertical profile covered by the plane (300m-10 km) and the ground based site (35m). The abstract is therefore correct.

4: Following the advice of reviewer 1 we have inserted the more up-to-date ACP Millet reference which was not available at the time of writing.

5: In order to reduce the number of references we refer to the review of de Gouw and Warneke, 2007

6: The background measurements were made by passing ambient air over the catalytic converter in order to maintain a consistent humidity between sample and background.

7: The instrumental description of the TD-GCMS has been shortened considerably.

8: As suggested by reviewer 1 the model results shown in Figure 2 have been revised to include only the model values after 1 day's simulation over the ocean at the coast. The generally low impact of biomass burning on the measurement area has been discussed elsewhere (Lelieveld et al. 2008, Stickler 2007). These works are now referred to explicitly in the text and we also discuss the low potential impact on our fluxes in the discussion section.

9: We would like to point out that MEGAN is an emission algorithm that prescribes only the emission of species e.g. isoprene but it is not itself an atmospheric model. This, and the recent agreement between flux measurements by Karl et al. with MEGAN estimates has been made clearer to the reader by the following sentences: "The oxidation chemistry of BVOCs over low NO_x Tropical ecosystems is currently not well understood. It is therefore important to compare in situ measurements and empirically derived fluxes with those predicted by models as there is evidence for large discrepancies reported between measured and modelled isoprene concentrations from these regions (Ehhalt and Prather, 2001; von Kuhlmann et al., 2004; Jöckel et al., 2006). These discrepancies seem to occur in all model simulations despite the use of well established isoprene emission algorithms (Guenther et al., 1995; Guenther et al., 2006). In

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

contrast, Karl et al., (2007) have recently reported good agreement between measured fluxes and those predicted by the emission algorithm MEGAN."

10: As requested by reviewer 1 individual profiles for several species over the rainforest are now provided in Figures 6 and 7. While these show a clear concentration jump in the isoprene profiles, alluded to by reviewer 1, they also show the day-to-day variability in the vertical profile and highlight that shallow convective mixing can on occasion mix isoprene slightly higher up. These points are now included in the discussion section.

11: The phrase has been rewritten for clarity. It now reads:"For this study, we'll focus on a transect which corresponds to the distance an air mass has spend between sunrise and sunset. In between, the column of air was advected with an average speed of 5.4 m/s over the rainforest, being exposed to the surface emissions between the east coast of French Guiana and the eastern shore of the reservoir (54.9 W)."

12: As suggested the paragraph in question has been rephrased and moved to a more appropriate position in the text (model initialization section).

13: The section on isoprene chemistry has been condensed by approximately by half and the suggested reference is cited.

14 : As requested average profiles in Figure 6 and 7 have been replaced by individual profiles, see point 10. The SCM does not use a flux estimate inferred from concentrations but calculates separately online from the simulated micrometeorology the isoprene fluxes according to Guenther et al. (1995) or Guenther et al. (2006). A companion study by Ganzeveld et al., (2008) shows the sensitivity of simulated reactive trace gas exchanges to the vertical resolution using a 60 layer version of the SCM. The difference between the 19 and 60 level model versions are now shown in the revised paper. This is a very valuable and interesting addition to the paper since it shows that the increase in resolution within the SCM effectively reduces boundary mixing ratios by circa 30%. This nicely highlights the sensitively of modelled ratios to the resolution of mixing.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



15: The fragmented discussion on the ratio (MACR+MVK)/ISOP has been merged into one section of the paper, namely section 5.6 as suggested.

16: At the time of submission the 60 level version of the model was in development. In the revised version, however, we now include the 60 level data to compare the effect of resolution changes in the simulated data.

17: Vertical profiles are now shown as function of the absolute altitude up to 6.5 km. The issue of biomass burning has been addressed under point 8, and previous papers, see above.

18: The text has been reorganised. The sentence merely refers the reader to the appropriate figure and has been amended appropriately.

19: No correction factor other than the humidity dependence of the PTRMS-calibration factor has been applied to either ground based or airborne datasets. The resulting mixing ratios measured at Brownsberg rise to maximum ~ 7 ppbv, whereas in the mixed layer maximum of ~ 4.5 ppbv has been observed. This is certainly a significant difference in contrast to reviewer 1's comment.

20: The overestimation of the MVK and MACR is partly the result of an underestimated chemical destruction of these isoprene oxidation products. However, as has now been highlighted by the comparison between the L19 and L60 versions of the SCM, the higher model resolution and better resolved mixing therein also leads to a clear improvement in the measurement/model comparison. See discussion section.

21: The sentence on line 22 of page 12929 has been rewritten for clarity and we include an extra Figure 10b to show the profile.

22 & 23: As suggested these points have been collectively addressed under section 5.6 in the revised text.

24: Has been corrected.

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

25: The reviewer is correct in interpreting the 'measured median flux' as the flux calculated from the median of each 15min interval of measurements. This is now stated in the text. We agree with the reviewer that the emission corrected for chemical loss and entrainment represents the best estimate.

26: The consistency check shows that when the mixed layer method is applied to other data collected on this campaign the fluxes are consistent with previous studies. We believe this supports the use of this method in this case, and hence we prefer to retain these two sentences.

27: We agree with the reviewer that it is difficult to distinguish between vertical transport and biomass burning in these circumstances. We have accordingly condensed the discussion on biomass burning referring to previously published papers (Stickler 2007 and Lelieveld 2008).

28: By showing the modelled OH (which expresses the state of knowledge of chemical and dynamical processes) to be lower than measured we show that the measured OH is higher than currently 'modelled', at least by the SCM model. To avoid confusion we have changed this sentence, replacing 'believed' with 'modelled'. The GABRIEL measurements are also discussed and presented in detail elsewhere Martinez et al., 2008.

29: We agree that the results in this study alone do not show that clouds and deep vertical transport influence the methanol and acetone vertical profiles. However, Large Eddy Simulations by Vilà-Guerau de Arellano et al., (2008) have indicated that this is indeed the case, however, we concede that this is beyond the scope of this paper and have removed this discussion, referring instead to the aforementioned work.

30: For the global extrapolation we have used the maximum rather than the daily average isoprene flux. We agree with the reviewer that this is not appropriate. This has been amended using the diel profile of emissions from the model. The maximum modelled isoprene emission flux (based on MEGAN) for this area is 14 mg isoprene

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

m-2h-1. Averaged over 24 hours, we calculate a daily average flux which is a factor of 4.8 lower. We have derived the global estimate by applying this factor to our measured maximum emissions, as in now explained in the text.

31: We have changed the word 'uncertainty' to 'sensitivity' for clarity.

References

de Gouw, J., and Warneke, C.: Measurements of volatile organic compounds in the earths atmosphere using proton-transfer-reaction mass spectrometry, *Mass Spectrometry Reviews*, 26, 223-257, 2007.

Ehhalt, D., and Prather, M.: *Atmospheric Chemistry and Greenhouse Gases, Climate Change 2001; Working Group 1: The Scientific Basis*, edited by: Houghton, J., Ding, Y., Griggs, D., Noguer, M., van der Linden, P., and Xiaosu, D., Cambridge University Press, 2001.

Ganzeveld, L., Eerdeken, G., Feig, G., Fischer, H., Harder, H., Königstedt, R., Kubistin, D., Martinez, M., Meixner, F. X., Scheeren, B., Sinha, V., Williams, J., Vilá, J., and Lelieveld, J.: Surface and Boundary Layer Exchanges of Volatile Organic Compounds, Nitrogen Oxides and Ozone during the GABRIEL Campaign, *Atmos. Chem. Phys.*, 8, 6223-6243, ISI:000260558500016, 2008.

Guenther, A., Nicolas Hewitt, C., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., McKay, W. A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, J., and Zimmerman, P.: A global model of natural volatile organic compound emissions, *J. Geophys. Res.*, 100, 8873-8892, 1995.

Guenther, A., Karl, T., Harley, P., Wiedinmyer, C., Palmer, P. I., and Geron, C.: Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature), *Atmospheric Chemistry and Physics*, 6, 3181-3210, 2006.

Jöckel, P., Tost, H., Pozzer, A., Brühl, C., Buchholz, J., Ganzeveld, L., Hoor, P., Kerk-

S12131

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



weg, A., Lawrence, M. G., Sander, R., Steil, B., Stiller, G., Tanarhte, M., Taraborrelli, D., van Aardenne, J., and Lelieveld, J.: The atmospheric chemistry general circulation model ECHAM5/MESSy: Consistent simulation of ozone from the surface to the mesosphere, *Atmos. Chem. Phys.*, 6, 5067-5104, 2006.

Karl, T., Guenther, A., Yokelson, R. J., Greenberg, J., Potosnak, M., Blake, D. R., and Artaxo, P.: The Tropical Forest and Fire Emissions Experiment: Emission, Chemistry, and Transport of Biogenic Volatile Organic Compounds in the Lower Atmosphere over Amazonia, *Atmos. Chem. Phys.*, 7, 5175-5196, 2007.

Martinez, M., Harder, H., Kubistin, D., M., R., Bozem, H., Butler, T., Eerdeken, G., Fischer, H., Gurk, C., Königstedt, R., Klüpfel, T., Lawrence, M., Parchatka, U., Schiller, C., Stickler, A., Williams, J., and Lelieveld, J.: Hydroxyl Radicals in the Tropical Troposphere over the Suriname rain forest: Airborne Measurements, *Atmos. Chem. Phys. Discuss.*, 8, 15491-15536, 2008.

Vilà-Guerau de Arellano, J., van den Dries, K., and Pino, D.: On inferring isoprene emission surface flux from atmospheric boundary layer concentration measurements, *Atmos. Chem. Phys. Discuss.*, 9, 4159-4193, 2009.

von Kuhlmann, R., Lawrence, M. G., Pöschl, U., and Crutzen, P. J.: Sensitivities in global scale modeling of isoprene, *Atmos. Chem. Phys.*, 4, 1-17, 2004.

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 8, 12903, 2008.

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)