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Atmospheric Chemistry and Physics Discussions

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.

Anonymous Referee #1

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This paper describes measurements of isoprene, methanol and acetone over the rain forest in the Guyanas during the GABRIEL aircraft campaign. VOC measurements over the Amazonian rain forest are still rather sparse; especially large-scale aircraft measurements are rare. This paper shows the diurnal and altitude profiles of some measured VOCs and calculates emission fluxes from those profiles. The results are compared to a single column model (SCM). The data and analysis presented here are an important contribution to the field and should be published, but I have various major comments that need to be addressed before this paper is publishable.

Major comments:

First of all, the paper seems very long for the results presented. The main data presented are altitude profiles, a diurnal profile from the aircraft and from a ground site and a flux estimate. I think this can be done in far less than 50 ACPD pages (text with references) and I will point out paragraphs that can be shortened in the minor comments section.

My main concern is with the use and the results of SCM model. The main result of this paper is the flux estimate of isoprene, acetone and methanol. To obtain this result the SCM is not actually needed, it is only compared to the SCM flux estimate. There seems to be a problem with the isoprene emissions modeling and possibly also with the isoprene chemistry. The emission flux is taken from the MEGAN model and to fit the measurements better the MEGAN emissions are arbitrarily divided by a factor of two in the SCM. MEGAN has been shown to be generally in rather good agreement with measurements, see Karl et al. A quantitative comparison of the SCM with measurements is therefore biased by at least a factor of two and therefore a lot less meaningful and important. The other problem is the low and rather unrealistic OH in the model. The measurements show up to an order of magnitude larger values, which is extremely important in this analysis; especially since the recent findings about OH-isoprene chemistry from the GABRIEL campaign. All of these serious issues need to be addressed before the comparison with the measurements is useful and I think this paper here is not the appropriate place for such a discussion and therefore I would almost suggest removing the SCM modeling from this paper, which would still leave an interesting measurements only paper.

The authors point out in the introduction that during GABRIEL simultaneous measurements of VOCs and OH were performed, but they don’t make much use of the OH measurements. In the last chapter, Eq 3 describes how the emission flux can be estimated from the isoprene and OH measurements and the mixed layer height (mixed layer technique), which seems to be the more commonly used method. An isoprene

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emission flux of 20-28 mg m-2 h-1 is stated as a result of this calculation, but no details are given. What are the values used, what is the time of day for this flux, is this with or without taking the entrainment into account? Eq. 3 could actually be used to estimate the emission flux along the flight track in the CBL. The emission flux determined with this method is about a factor of 3-4 larger than with the CBL-BA method. This large discrepancy needs to be discussed. It is unlikely that the difference is due to mixing, because the diurnal profile used to calculate the emission flux from the aircraft measurements is a regional average and horizontal mixing is averaged out.

The intercomparison of the PTR-MS with the GC-MS shown in Figure 1 results in 25% lower PTR-MS values and the data are corrected for this difference. The authors blame the difference on the dry calibration of the PTR-MS. This needs to be checked in the laboratory measurements before a data correction can be made. PTR-MS might detect other compounds on this mass, which would result in an over-estimation not an under-estimation. GC-MS analysis of cartridges relies on rather complicated sampling procedures and is known to be sensitive to various sampling artifacts. PTR-MS on the other hand is a very direct technique and recent inter-comparisons have shown that PTR-MS performed more quantitative than GC analysis of cartridges in chamber experiments. Therefore the data should not be corrected for the difference, if it is not possible to correct for humidity with laboratory experiments. The other problem with Figure 1 is that only few data points are plotted. All the 62 cartridges need to be shown. Were the fits done through the plotted data or all data? Furthermore, please remove the confidence and the prediction band as they are not important and clutter the Figure unnecessarily.

Minor comments:

Throughout the manuscript are multiple spelling and grammar mistakes that need to be corrected.

Abstract: What is consistent with global emissions, the SCM with MEGAN*0.5? The

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SCM is only a local model, how can it be consistent with global emission estimates.

Abstract: The exchanges of methanol and acetone can be reasonably well described with the compensation point approach. This was not really shown in the manuscript.

Abstract: The text suggests that the Learjet flew profiles as low as 35m. I assume the authors talk about the ground site here.

Page 12906: Jacob et al reference was updated recently by Millet et al. ACPD

Page 12908: The four PTR-MS references can be replaced by the recent review by de Gouw and Warneke, 2005

Page 12910: Were the background measurements through the catalytic converter done with dry air? This would influence especially the methanol background.

Page 12912: The GC measurements were only used in the inter-comparison in Figure 1 and therefore the instrument description does not need that much detail and should be shortened substantially.

Page 12917: The vertical profiles over the ocean in Figure 2 have a clear maximum in the free troposphere with about 160 ppbv of CO and 250 pptv of acetonitrile, which suggests clear influence of biomass burning. This is very important for the determination of the emission fluxes of the longer lived VOCs acetone and methanol, when the entrainment is taken into account. If the measured VOC profiles shown are used to initiate the SCM model, why are model results also shown in the graph?

Page 12917: It should be mentioned here that Karl et recently found a rather good agreement of isoprene flux measurements with MEGAN over the Amazonian rain forest and not a factor of two overestimation as does the SCM.

Vertical profiles Figure 2, 3, 6 and 7: All vertical profiles shown here averages even though all the measurements are high time resolution. A very long discussion about the boundary layer conditions and mixing is given in chapter 5.1. It is very important

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for the presented analysis if the VOCs are well mixed through the boundary layer and if the gradient between the boundary layer and the free troposphere is well defined. This cannot be seen in averaged profile but need to be shown in individual ones. Showing individual profiles can shorten much of the discussion in chapter 5.1. The section also discusses boundary layer height estimates, but it is not clear what is used in rest of the manuscript; especially in Section 5.4. Here again individual profiles of isoprene will show to what heights isoprene is mixed up to.

Page 12922: I do not understand the sentence starting: With an average wind speed;

Page 12922 last paragraph: What is meant by simulated mixing ratios are based on emission fluxes that are inferred from the airborne measurements. It is not really discussed in chapter 5.7. Please explain and reorganize, because this should not be in a section called data selection criteria.

Page 12923: The isoprene chemistry discussion is rather long and should be shortened. The concept of a conserved isoprene tracer was used recently be de Gouw et al 2005 and could be quoted to shorten the discussion.

Page 12924: How many profiles are used in Figure 6 and 7? Again it is not clear if isoprene is well mixed throughout the boundary layer because of the averaging of multiple profiles. It is clear that the SCM model does not mix isoprene well certainly less than the measurements indicate. What does that mean for the flux estimates in the SCM? In Sect. 5.7 two SCM levels are averaged what error will that produce?

Page 12924-12925: The isoprene/MVK+MACR is discussed in detail here and elsewhere in the manuscript. This should be done only in one place in the manuscript, please reorganize and move the discussion to Sect. 5.6.

Page 12925: If a higher vertical resolution version of the SCM is available and gives better results, why is that version not used here. It is very unusual not to use the best available results.

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Page 12926: In Figure 7 the altitude profile goes up to 3.0, but the text discusses levels of 4-5 is discussed. Please show the full profile. The measurements show a methanol and acetone maximum at 1.5-2.5 and by looking at the profile in Figure 2 it seems that the free troposphere is influenced by biomass burning. This possibility needs to be discussed and clarified.

Page 12926 line 14: This sentence cannot be understand without Sect. 5.7. This should be reorganized.

Page 12927: The ground based measurements don't seem to be significantly higher than the airborne measurements, there seems to be a difference of about 1-2 ppbv. Here again the correction factor for the PTR-MS data should not be applied for the ground based measurements.

Page 12928: It is really strange that the SCM model overestimates isoprene and MVK+MACR in the afternoon. With the low OH in the model isoprene should be higher, but the oxidation product certainly should not.

Page 12929 line 22: I don't understand: constantly increasing ratio between sunrise and sunset without increase after twelve. Please reformulate.

Page 12929: Here again the MVK+MACR/isoprene ratio is discussed, which should be moved to the next section.

Section 5.6: In this section the MVK+MACR/isoprene ratio should be discussed. In general this section is hard to understand without a figure: the diurnal profile of the MVK+MACR/isoprene ratio, the photochemical age and lifetime should be plotted. The altitude profile should be moved here.

Page 12934 line 8: Eq.2 is not correct it should be section 5.3.

Page 12935-12936: What is meant by: measured median flux? Looking at Figure 11, I assume it is the maximum in the diurnal profile. The first paragraph gives flux estimates without entrainment or chemical compensation and for different boundary

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layer heights. It is not stated what the authors think the actual emission flux is and why. Earlier it was stated that the emission flux is estimated by correcting for chemical loss using the conserved tracer isoprene+MVK+MACR+others, the entrainment is certainly important, so I would assume that 8.7 mg m-2 h-1 is the best estimate. Please clarify.

Page 12935: The consistency check with CO2 should be removed, as it does not add any value to the isoprene flux comparisons with other measurement studies.

Page 12940: The vertical profiles of acetone and methanol might be influenced by biomass burning and therefore deeper transport into the troposphere is very difficult to assess with this data set.

Conclusions first paragraph: The measurements of VOCs and OH presented here do not actually show that OH is higher than currently believed. This sentence should be removed.

Page 12942: I also do not agree that the results in this manuscript show that cloud driven vertical transport has consequences for acetone and methanol in the free troposphere.

Page 12942: How is the global scale emission flux estimated? Multiplying 7.3 mg m-2 h-1 with 11e6 km2 yield about 620 Tg/year, but 7.3 is the daytime maximum and the actual emissions might be about a factor of four lower. What is the MEGAN tropical rainforest emissions estimate?

Page 12942 line 19: I do not understand this sentence. To estimate the uncertainty in emissions a deeper mixed layer is applied. Please rewrite this sentence.

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

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