Atmospheric Chemistry and Physics Discussions

Interactive comment on "Improved simulation of isoprene oxidation chemistry with the ECHAM5/MESSy chemistry-climate model: lessons from the GABRIEL airborne field campaign" *by* T. M. Butler et al.

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Review of "Improved simulation of isoprene oxidation chemistry with the ECHAM5/MESSy chemistry-climate model: lessons from the GABRIEL airborne field campaig", by Tim Butler and co-authors.

This paper deals with measurements of Isoprene and other reactive compounds over the tropical rain forest in South America. Special emphasis of the GABRIEL campaign is on the measurement of the OH radical in combination with Isoprene. Global atmo-

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spheric chemistry models have problems to account for the large isoprene fluxes that are inferred from field measurements. Due to the high reactivity of isoprene towards OH, modeled OH concentrations drop, thereby increasing the Isoprene lifetime. To avoid a positive feedback loop (lower OH, more isoprene, etc.) most models reduce the Isoprene emissions. According to the authors, the GABRIEL measurements now show that the OH concentrations are not reduced compared to "normal" values. Moreover, the observed isoprene concentrations are lower than the modeled concentration. The authors first tackle this intriguing problem by assuming that OH is recycled in the OH + Isoprene reaction. The recycling efficiency has to be adjusted to 40-50% which leads to modeled OH concentrations close to observed values. Now, however, another problem appears: the modeled isoprene concentrations fall below the observed values. This cannot be remedied by increasing the isoprene flux since that would lower the OH again. As a last try, the authors play with the rate constant between Isoprene and OH. When the rate is reduced by 50% (implying an intensity of segregation of -0.5) a "best fit" with observations is obtained. This engineering atmospheric chemistry may lead to a better understanding of fundamental processes. This paper, however, has many methodological shortcomings. Moreover, I think the authors want to show too many results and the paper would be better of when focused on the boundary layer only.

It seems there are references to other papers in preparation (Eerdekens et al., Martinez et al., Taraborrelli et al., and Kubustin et al.) that appear to deal already with the same problem on the smaller scale (Box models). The main findings are already published in the Lelieveld et al. Nature paper that appeared last week. It seems problematic to me to publish another paper that specifically deals with the global implications, since so little is understood on the local and regional scales.

Thus, although impressive in the amount of computational effort spent, the paper should improve considerably in my opinion. Hopefully, the detailed comments below help the authors to find ways to present their main findings in a clearer way.

For the moment, I refrain from more detailed comments (language and small issues)

since I think the paper requires first a better focus.

Main concern: Too many too small pictures.

Figures 4-10 present 9-panel figures with too small letters, and color-coded height. These figures are difficult to read and distract from the main issue. Why not select 0-2000m only? Here the problem appears most clearly. When I zoom in on my screen (600%) and focus on the blue dots only, figure 4 shows modeled isoprene values of 2-3 ppb and observations that range from almost zero to more than 5 ppb. In general, there indeed seems to be an overestimate in the model (the main focus of the paper), but the situation appears extremely variable. OH (blue dots only) is underestimated by the model, but not always. A first question that pops up: Is OH underestimated when isoprene is overestimated? Later in the paper a dimensionless co-variance of -0.1 is quoted, indicating that this is not a predominant issue. However, the second important question is: What then brings observed OH down compared to the modeled value? These fundamental questions are now lost in a mist of plots. The problem calls for steady-state considerations of OH (not mentioned in the paper) and analysis of the isoprene variations (fresh emissions in updrafts, low concentrations in downdrafts due to entrainment from the free troposphere?). Now the correlations between species play a minor role in the presented discussions, but ultimately may provide clues (a lot of HCHO in aged air with less isoprene?). Admittedly, the situation is complex, and meteorological measurements (e.g. vertical winds) virtually absent, but the current analysis fails to deal with these questions.

Another issue: do you understand the poor model performance for CO?

In figure 4 (blue dots only) measurements show values between 80 and 220 ppb, while the model values lie between 100 and 120 ppb. With isoprene replaced by CO emissions (figure 6) the modeled values range from 120 to 240 ppb (now a considerable overestimate). The paper mentions: "although there are differences in the vicinity in the isoprene source regions" (page 6282). These differences are large in my opinion and

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tell something about the system. Isoprene or other intermediates in the isoprene-CO oxidation chain are taken away from the system, most probably by transport. Sensitivity to transport is hardly covered by the paper. And transport to the free troposphere may proceed fast when shallow/deep cumulus clouds are present. And when isoprene emissions are faster mixed in the environment, the OH draw-down probably is less of an issue. So I miss sensitivity calculations that deal with (vertical) transport.

Figure 2: show the right quantity

Figure 2 intends to show that the primary OH production is well modeled. To that end, O3, JO3 and H2O comparisons are shown. The authors should consider the analysis of the product: O3.JO3(eff).H2O, which is the correct measure for primary OH formation. I do not know whether these terms are measured simultaneously, though. The large spread in JO3 in the PBL indicates that clouds are present, I assume?

Figure 7: sorry, unreadable

I am strongly in favor of budget analysis. Presented in the form of figure 7 and stating (page 6284): "Clearly there is a trade-off.." grossly overestimates the eye-sight of many potentially interested readers. Too much information (why the whole troposphere?) in too little space. Focus on the point you want to make!

Intensity of segregation

The authors present an analysis of the intensity of segregation between Isoprene and OH. There are several mechanisms that may lead to segregation of reactants in e.g. the PBL and I think these processes are not well separated in the analysis. The lifetime of Isoprene is sufficiently short to result in considerable concentration differences in the PBL. On the one hand, updrafts (indeed not resolved in the global model) carry isoprene rich air in which OH concentrations are suppressed. Downdrafts, on the other hand, may be relatively depleted in isoprene (not having seen fresh emissions for a while) and may be relatively enriched in OH. For the understanding of the reader it is

essential to notice that OH in models is not a transported quantity. That means that the local OH concentration is governed by the longer living species that produce and deplete OH. With OH production terms P (molecules/(cm3.s)) and OH lifetime L (1/s), OH is assumed in steady state (OH = P/L). When in the original isoprene oxidation scheme L is dominated by isoprene, the variance in the measured isoprene concentrations can be used to determine the segregation between OH and Isoprene directly. In fact, measurements of the entire chemical composition of an air mass, including OH, could provide important clues about the magnitude of the OH recycling term: steady state OH should be identical to measured OH. If steady state OH is too low, either L is too large or P is too small (implying recycling). In fact, such a chemical budget analysis formed the basis of many earlier measurement campaigns in clean environments. Heterogeneous emissions of isoprene will normally enhance the spatio-temporal variance of the isoprene concentration and hence lead to a more pronounced segregation of isoprene and OH. Of course, OH variations are not determined by isoprene only and that is why measurements of primary production, OH recycling (e.g. by NO), and OH reaction partners (CO, other hydrocarbons) are so important. Luckily the measurements are there and wait for analysis!

Global Implications

A good reason to use a global model for the analysis would be the quantification of the effect on a global scale. What are the implications for the methane lifetime? Such an analysis is not given. Instead, the authors performed a four year integration and compare the model output to earlier measurement campaigns. Many questions arise again that are interesting but deserve a more thorough discussion than can be given in this paper (again: too many subjects). My impression is that the global implications (e.g. on the methane lifetime) are small. The recent Nature paper (Lelieveld et al., 2008) also lacks these relevant numbers. A quick try: yearly emission of 600 Tg-C isoprene represents about 10 Tmol, and when 2 extra OH molecules are formed (eq. 2) this would imply 20 Tmol OH, which seems non-negligible in the global OH budget?

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