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Atmospheric
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Interactive comment on "Impact of biogenic hydrocarbons on tropospheric chemistry: results from a global chemistry-climate model" *by* G. A. Folberth et al.

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This is a very interesting paper that presents both a comprehensive validation of an impressive new tropospheric chemistry model with detailed hydrocarbon chemistry, and an interesting scientific study on the effects of biogenic hydrocarbons on the chemistry of the troposphere. Both the validation and the scientific study are treated well and the two together make a nicely balanced paper. Naturally I have some criticisms, but I hope they won't be too difficult to address, as this paper should certainly be published.

Specific comments 1) Section 3 : Methane seems to be free-running in this model

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rather than fixed, however there is no discussion of its concentrations. It is claimed that methane is in equilibrium so it would make sense to compare the model concentrations with observations. I appreciate that there may be an offset between the model and the observations, but a comparison would still be instructive. There doesn't seem to be any methane dry deposition in table 1. Dry deposition of methane (consumption by methanotropic bacteria in soils) is about 30 Tg/yr (IPCC 2001).

2) Section 3.4 The discussion of the formaldehyde concentations focusses on pollution or biomass burning sources. Isoprene degradation is a large source of isoprene, and agreements/disagreements between model and observations could be a useful test of the isoprene emissions. The authors would have to be sure they were looking at regions remote from isoprene sources before they could use formaldehyde measurements to comment on their anthropogenic or biomass burning sources.

3) Section 3.5, pages 10540-10541 It is surprising that adding NMHCs increases the strat-trop exchange. Since the downward flux of ozone should be the same, does this imply that the upward flux has decreased? I don't think it tells us anything to claim that net chemical production is 75% of the STE. Net chemical production is just equal to Ddep-STE, so the calculation is then: (Ddep-STE)/STE=0.75. The uncertainty in this is huge, if the STE was 523 as in the CH4-only version the Net chemical production/STE fraction would be 140%. If this fraction were relevant (I think it isn't) this would imply that the Ch4-only version had more ozone production than the NMHC one.

4) Section 4.1, page 10543 This section also needs to include a mention of the differences in isoprene emissions in January and July (magnitudes and distribution). The importance of NOx over the eastern US is mentioned, but there is a more general point to be made about the coincidence of isoprene and NOx sources in July and a separation of isoprene and NOx sources in January.

5) Page 10545 Again, in the PAN discussion the coincidence or separation of isoprene and NOx sources should be discussed.

6) Page 10546, lines 6-10. Should comment that methacrolein and formaldehyde have short lifetimes, so would need to be transported by convection to the free troposphere. I would have expected the photolysis of MACR and HCHO to generate HOx. I would be interested to know whether total HOx has increased in the mid-upper troposphere, even though OH has decreased. I would recommend that figure 16 is replaced by O3, CH2O, OH and HOX zonal plots as in figures 19 and 20.

7) Page 10546, line 17 I would have thought that the extra NOx could increase OH on its own though altering the HOx partitioning. Are the authors sure the effect is due to ozone?

8) Page 10546, lines 22-24 It is interesting that the fractional decrease in methane lifetime (˜4%) is a lot less than the fractional decrease in OH (˜10% in line 13). This is surprising since the region of greatest methane destruction is in the tropical lower troposphere where the OH decreases seem to be largest. This should be commented on, and if possible, understood further.

9)Page 10547 This work on MVK/MACR ratios is very interesting and will give useful scientific conclusions, but the analysis needs a little more work on it. Apel et al. indeed quote a ratio of 1.4, but note this is a production ratio and not a concentration ratio. It is not clear from their paper, but I assume this ratio is for the isopO2+NO reaction. However in the reaction scheme in this paper (k113 in table 4) the ratio is 0.354/0.404=0.9 . I am not expert enough to know which of these ratios is more realistic, but for the purposes of this paper the value of 0.9 should be used (it would be helpful if the colour scale in figure 18 could be chosen to pick out this contour). Von Kuhlmann et al. ACP 2004 have a good description of the effects of different isoprene schemes.

How exactly are the annual mean MVK/MACR ratios calculated? Are the ratios calculated every timestep and then meaned over the year, or are the mean annual concentrations calculated and then the ratio taken? This is important since it affects the relative weighting of the day and night-time values. If the concentrations are averaged over a period of 24hrs or more, then the higher concentrations during the daytime will weight the results more towards the day than the night. If the ratios are calculated over a period of 12hrs or less, then day and night will be equally weighted even though the daytime is more important for isoprene oxidation. I am rather sceptical that over South America, most of Africa, and South East Asia, the isoprene oxidation from ozone and NO3 is as important as from OH. These are areas of very high OH concentrations, but not that large ozone (or NO3) concentrations. Ozone and NO3 could seem to be important if the ratios were calculated more frequently than daily since this would give equal weighting to the night-time oxidation (which is mostly through ozone). Another (I think more likely) explanation is that most of the isoprene is oxidised by OH, but that the different MVK/MACR ratios reflect the subsequent reactions of the isopO2 radical.

k113 isopO2+NO: ratio=0.88

k115 isopO2+HO2: ratio=0.85

k116 isopO2+CH3O2: ratio=0.58

k117 isopO2+CH3CO3: ratio=0.59

Thus when there is sufficient NOx, the production ratios are around 0.9, but if the isoprene degredation is through peroxy-peroxy recombination then production ratios may come down to 0.6. As the authors say, this ratio will increase due to the differing lifetimes of MVK and MACR.

It is confusing the picture (particularly in the extra-tropics) to show an annual average plot, since the winter values (according to hemisphere), which are not so important, will skew the results. January and July plots need to be shown instead. If the authors have reaction fluxes output from these model runs, they would be useful to ascertain the most important routes for isoprene oxidation and subsequent reaction of isopO2.

Technical comments

page 10521, line 3: add a reference to Sanderson et al. JGR 2003.

page 10525, line 19: "note" -> "not"

page 10525, line 20: "note" -> "not"

page 10526, lines 4-9: Is the decision on which solver to use for which species made global, or for each grid point? Is it made every timestep? If it is made globally, for all time, then the species should be listed here.

page 10532, line 13: "constraint" -> "constrained"

page 10533, line 21: Should state that the 9.2 years refers to the lifetime due only to OH removal.

page 10534, line 23: "significantly"->"significant"

page 10535, line 25: "reproduces"->"reproduce"

page 10536, line 3: "well"->"reasonably well"

page 10536, line 25: "ratio"->"ratios"

page 10544, lines 1-2: "forcing of ozone"->"forcing of ozone due to isoprene emissions" page 10544, line 7: "Apparently, isoprene"->"Isoprene"

page 10544, line 28: "100 pptv"->"50 pptv"

page 10545, line 8: "seems to be"->"is"

page 10547, line 11: "isoprene"->"isoprene and its products"

page 10547, line 15: "Apparently large"->"Large"

page 10551, lines 20-21: Dry dep of methane is roughly of equal importance to stratopsheric destruction.

page 10554, line 8: "Carbon monoxide"->"Compared with a no-isoprene run, carbon monoxide" page 10554, line 10: "The key role of"->"An important role of"

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 10517, 2005.