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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.

Anonymous Referee #2

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The article describes a 3-d global-scale chemistry/transport model, used here to evaluate (mainly) gas-phase photochemistry. Extensive comparisons are shown with a wide range of measured ambient concentrations, and global budgets for tropospheric O3, reactive nitrogen and CO are discussed. The title is somewhat misleading: The article does describe the impact of biogenic hydrocarbons on tropospheric chemistry (by comparing results with and without isoprene, acetone and methanol), but it is more useful as a broad summary of the current state of tropospheric chemistry. It is a useful article and worth publishing.

It is noteworthy that the results seem to converge with results of several other tropospheric models (most of which are discussed in the article). In terms of major results (e.g. oxidizing capacity, relative role of in-situ photochemistry versus transport from the stratosphere as sources of tropospheric ozone), the results here differ from others by 20% or less. The manuscript does not describe any major differences between results obtained here and results from different models, which might be used to evaluate different assumptions in different models. Consequently, the results of this model may be viewed as the current consensus concerning tropospheric chemistry.

Specific comments:

The isoprene reaction sequences involving RO2+HO2 are especially important for assessing the global impact of isoprene. Most isoprene is emitted in low-NOx environments, so the degradation of isoprene and its major products (methylvinyl ketone and methacrolein) occurs largely through the reaction of RO2 radicals with HO2 (forming organic peroxides) rather than with NO. The subsequent reaction pathways are not well understood.

Here, the RO2+HO2 reactions for isoprene and related species (Table 4, k115, k144, etc.) are derived from a Ph.D. thesis (Brocheton, 1999), which is not widely available. These reaction sequences deserve more attention in general (not just in this paper). Isoprene-RO2+HO2 produces a hydroperoxide, but this is represented in the model only by a counter species (XOOH) and the products of subsequent breakdown of peroxides. This raises several questions. The atmospheric lifetime of hydroperoxides may be longer than either isoprene or its immediate reaction products (methylvinyl ketone and methacrolein). By assuming that the hydroperoxides react instantaneously, the mechanism is effectively shortening the lifetime of the volatile organic content of isoprene. The possible deposition of hydroperoxides may also affect this representation. I suggest that some discussion of this uncertainty be added to the text.

The article contains an excellent suggestion concerning the use of ambient ratios be-

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tween MVK and methacrolein to evaluate the role of isoprene peroxides. Further investigation of this is probably beyond the scope of the current paper.

Production of hydroxyalkyl nitrates from isoprene represents another area of uncertainty. The chemistry used in this article (Table 4) has a high yield of organic nitrates from the isoprene RO2+NO reaction (12%), and the subsequent breakdown of lumped organic nitrates (ONITR, reactions k175 and k176 in Table 4) does not yield reactive nitrogen. Thus, formation of hydroxyalkyl nitrates represents a sink for reactive nitrogen (and also for organics). This tends to minimize the impact of isoprene as an ozone precursor (since removal of reactive nitrogen reduces subsequent ozone formation. Poschl et al. [2000] and von Kuhlman et al. [2004] found that this assumption has a significant impact on ozone and nitrogen chemistry (up to 20%). I suggest noting these uncertainties in the text.

The overall impact of isoprene in the model is comparable to the estimate from Horowitz et al. (J. Geophys. Res., 1998).

The text refers to the global warming potential of 0.09 W/m2 from isoprene due to the increased O3. Subsequently, the text notes that isoprene also lead to lower OH and a longer lifetime for CH4. It would be useful if the global warming potential could also be given for this indirect effect.

Minor corrections:

p. 10520: “principle” should be “principal”. p. 10525: “note included” should be “not included”.

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