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Comment

Interactive comment on “The Chemistry of Atmosphere-Forest Exchange (CAFE) Model – Part 1: Model description and characterization” by G. M. Wolfe and J. A. Thornton

D. Taraborrelli (Referee)

domenico.taraborrelli@mpic.de

Received and published: 19 October 2010

General comment

The manuscript present a 1-D chemical transport model for the gas exchanges between the atmosphere and the forest. The nature and the focus of the model fall well within the scope of ACP as it combines many processes from radiation to trace gas emission/deposition, from turbulent diffusion to photochemistry. The manuscript is well written. The description and discussion of parameterizations are very informative.

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From my point of view the main novelty of the model presented here consists in the implementation of a subset the Master Chemical Mechanism that was extended and modified to include higher terpene chemistry and epoxides from isoprene. Here, most of these changes are reviewed critically and a series of modifications is considered necessary (Major comments). I recommend publication of the manuscript after the following requests are accepted and the comments properly answered. At the end of this review there are a number of suggestions that, if adopted, will likely improve the model ability to reproduce the BEARPEX-2007 results.

Major comments

- Epoxide chemistry

The tentative simplified dihydroxyepoxide chemistry by Paulot et al(2009a) is adopted. However, the reaction $\text{IEPOXO}_2 + \text{HO}_2$ unrealistically yields 1.125 OH. The study of Butkovskaya et al(2006) provides some evidence for only 0.125 OH that results from the reaction of O_2 with the HOCHCHO radical from HOCH_2CHO reaction. For consistency, $\text{HOCH}_2\text{CHO} + \text{OH}$ reaction should be changed as well. In many reactions the HOCH_2CO_3 radical is produced. For consistency, HOCH_2CO_3 should be substituted with the HOCH_2CO radical that undergoes decomposition upon reaction with O_2 as quantified by Butkovskaya et al(2006).

Furthermore, there is no experimental evidence (that I am aware of) for an OH-yield of 1 for the $\text{IEPOXO}_2 + \text{HO}_2$ reaction via a mechanism similar to the one for $\text{CH}_3\text{CO}_3 + \text{HO}_2$. In fact, this was assumed "for simplicity" by Paulot et al(2009b) (F. Paulot, pers. comm.). A way out for the authors would be to assume that $\text{IEPOX} + \text{OH}$ reaction proceeds via the mechanism described labeled as SR7c in the SOM of Paulot et al.(2009b). When considering the epoxide resulting from $\text{ISOPBOOH} + \text{OH}$ the major products should be the peroxy radicals C57O_2 and C58O_2 , already present in the MCM mechanism subset for isoprene. A similar choice was done by Archibald et al(2010).

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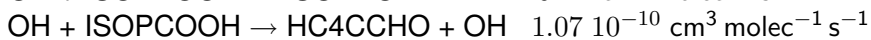
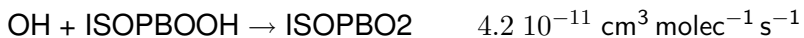
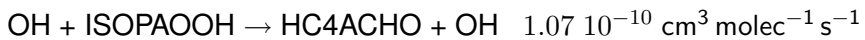
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- ISOPOOH + OH reactions

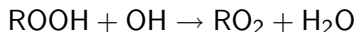
Paulot et al(2009b) used two reaction channels for OH + ISOPOOH (sum of A, B, C and D isomers) with the corresponding estimated rate constants. One channel produces the epoxide and the other one recycles 30% OH and forms 70% of the original ISOPO2. If this simplified scheme is adopted, the MCM reactions



should not be considered any longer. From the text and Table 6 it looks like these reactions were kept and not replaced. Then the authors use the second channel by Paulot et al(2009b)



only for ISOPBOOH that ironically is the only isomer that cannot recycle OH that way. In this case the -OOH group is on a tertiary C atom with no H-atom to abstract. HC5 is likely what in MCM is called HCOC5 and it is related to ISOPDO2 and not to ISOPBO2. Furthermore, the authors retain the rate constant $4.2 \cdot 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ for this reaction that is unrealistically high for this channel. The reaction channel



should be considered for each ROOH isomer and the corresponding rate constant should be similar to the one for CH_3OOH that is $0.6 \cdot 5.3 \cdot 10^{-12} \cdot \exp(190/\text{temp}) \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ (IUPAC Data Sheet HOx VOC34). In fact, Paulot et al(2009b) used the expression $3.8 \cdot 10^{-12} \cdot \exp(200/\text{temp}) \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ that is the previous IUPAC recommendation for $\text{CH}_3\text{OOH} + \text{OH} \rightarrow \text{CH}_3\text{O}_2 + \text{H}_2\text{O}$ reaction.

- Monoterpenes kinetics

In Table 6 an extension of MCM with partial chemistry of monoterpene and sesquiterpene is attempted. For both rate constants and product yields Atkinson and Arey (2003a) is cited although the rate constants were explicitly reported in Atkinson and Arey(2003b). This second source should be cited as well. Regarding myrcene and α -terpinene reaction with OH, Hites and Turner(2009) and Peeters et al(1999) reported measured rate constants that are about 30% higher than recommended by Atkinson and Arey(2003b). Actually the latter goes back to Atkinson et al(1997). Moreover, in Table 6 the rate constant of α -terpinene with O_3 should be $2 \cdot 10^{-14}$ (Atkinson and Arey(2003b)) and not $1.4 \cdot 10^{-16} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ as for γ -terpinene. In the companion manuscript the authors show that the model overestimates the mixing ratios of myrcene and alpha-terpinene and the new rate constants will significantly decrease the model-measurement discrepancy.

The average acetone-yield from myrcene + O_3 reactions should be about 25% and not 20% (Atkinson and Arey (2003a)). Why has a 20% yield been chosen?

- MBO chemistry

The MCM rate constant for the MBO + OH reaction has no temperature dependence and is about 10% higher than what recommended by IUPAC at 298K, $8.1 \cdot 10^{-12} \cdot \exp(610/temp) \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$. In fact, its rate constant should change by about 10% between cold and hot periods during BEARPEX. Considering that MBO is the most abundant VOC during BEARPEX contributing to the OH-reactivity the most, it is fair to expect a significant effect on the model results when the IUPAC recommendations are used.

Minor comments

In the manuscript the authors state that their model is the first of its kind to incorporate the Master Chemical Mechanism (MCM). I am afraid this is not true. I am aware of

at least another model (SOSA) whose description manuscript has already received positive reviews in ACPD (Boy et al., ACPD 2010) and will likely published earlier than the present manuscript.

In Sec. 3.7 and Tab. 6 the authors refer to Hasson et al(2004) for the 44% OH-yield in three $\text{RCO}_3 + \text{HO}_2$ reactions. However, the number 44% is the average OH-yield for the $\text{CH}_3\text{CO}_3 + \text{HO}_2$ reaction studied in another two labs (Dillon and Crowley(2008), Jenkin et al(2007)). This average value is recommended by IUPAC (Data Sheet HOx VOC54). Although the authors do not mention the yields for the other two channels of $\text{RCO}_3 + \text{HO}_2$, I assume that they are as the ones recommended by IUPAC, that is 15% and 41% for the $\text{RCO}_2\text{H} + \text{O}_3$ and RCO_3H channels, respectively. For the sake of clarity, it would better to mention all of this in the manuscript.

In Section 3.9 little is mentioned about the chemistry operator. I wonder in which format the MCM subset was downloaded. Considering the significant modifications to the mechanism, I imagine the format is probably the user-friendly format used by Kinetic Pre-Processor (KPP) (Sandu and Sander, 2006). Was this the case?

Suggestions for further changes

In light of the use the authors make of the CAFE model (see companion manuscript), the following suggestions for changes to the chemical mechanism may significantly improve the model results.

- Alkyl nitrates

Paulot et al(2009a) determined 11 and 15% yield for the alkyl nitrates from MVK and MACR OH-initiated oxidation. The MCM considers only a very small yield for the minor RO_2 isomer resulting from the $\text{MVK} + \text{OH}$ reaction. A simplified chemistry for these two alkyl nitrates could be taken from Paulot et al(2009a). Inclusion of the new alkyl nitrate yields may significantly improve the underestimation of the alkyl nitrate as shown in the companion manuscript.

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- CH₃CO₃ production and PAN

According to Baeza-Romero et al.(2007) the CH₃CO₃ yield from MGLYOX + OH reaction is 0.6. Furthermore, the study by Orlando et al(1999) suggests that the degradation of methyl-vinyl radical (represented in MCM by the decomposition reaction of MACO2) produces only 0.35 CH₃CO₃ under high-NO_x conditions. LaFranchi et al(2009) took it into account in their PAN budget analysis for BEARPEX 2007. In the companion manuscript the authors state that PAN is overestimated by 60% during hot days and this may help in reducing the discrepancy. Finally, the rate constant for the PAN + OH reaction in MCM is about 3 times higher than the upper limit recommended by IUPAC ($3 \times 10^{-14} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$).

- MBO chemistry

2-hydroxy-2-methylpropionaldehyde (IBUTALOH) is a major product of MBO oxidation. Its chemistry has been studied by Carrasco et al(2006) and it is quite different from the one implemented in MCM. First of all the IUPAC recommendations (Data Sheet HOX VOC33) for the rate constant of IBUTALOH + OH is 36% lower than in MCM. Second, the PAN-like compound, called C4PAN5 in MCM (Table A1), could not be detected. This agrees with theoretical predictions of Mereau et al. that the potential precursor of C4PAN5, the excited acyl radical resulting from IBUTALOH + OH, decomposes losing a CO molecule. Therefore, C4PAN5 is likely not formed during MBO degradation. In my opinion the IPRHOCO3-related species should not be present in the mechanism. This has significant implications for the overestimation of the total peroxyacyl nitrates showed in the companion manuscript.

Technical corrections

p.21653, l.17: "affect" should be "effect"

References

Archibald et al., 2010, DOI:10.5194/acp-10-8097-2010

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Atkinson and Arey, Atmospheric Environment, 2003a
Atkinson and Arey, Chem. Rev., 2003b
Atkinson, J. Phys. Chem. Ref. Data, 1997
Baeza-Romero et al., 2007, PCCP, DOI:10.1039/b614502g
Boy et al., ACPD, 2010, DOI:10.5194/acpd-10-18607-2010
Carrasco et al., Atmospheric Environment, 2006,
DOI:10.1016/j.atmosenv.2005.11.042
Dillon and Crowley, ACP, 2008, DOI:10.5194/acp-8-4877-2008
Hites and Turner, Int. J. Chem. Kin., 41, 407-413, 2009
LaFranchi et al., ACP, 2009, DOI:10.5194/acp-9-7623-2009
Jenkin et al., PCCP, 2007, DOI:10.1039/b702757e
Mereau et al., PCCP, 2001, DOI:10.1039/b105824j
Orlando et al., GRL, 1999, DOI:10.1029/1999GL900453
Paulot et al., ACP, 2009a, DOI:10.5194/acp-9-1479-2009
Paulot et al., Science, 2009b, DOI:10.1126/science.1172910
Peeters et al., Chemosphere, 38, 1189-1195, 1999
Sandu and Sander, ACP, 2006, DOI:10.5194/acp-6-187-2006

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 21721, 2010.

ACPD

10, C8885–C8891, 2010

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