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Atmospheric Chemistry and Physics Discussions

ACPD

13, C7398–C7402, 2013

Interactive Comment

Interactive comment on "The impact of the chemical production of methyl nitrate from the NO + CH_3O_2 reaction on the global distributions of alkyl nitrates, nitrogen oxides and tropospheric ozone: a global modeling study" *by* J. E. Williams et al.

Anonymous Referee #1

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General comments: The present paper reports a series of modeling experiments that aim to assess the potential importance of a recently reported (Butkovskaya et al., 2012) chemical production mechanism for the formation of methyl nitrate. Further model simulations assess the impact of a range of assumptions about physical loss and primary emissions of methyl nitrate, on the abundance of methyl nitrate and the impact on other trace gases in the troposphere. Comparison of the results of the model simula-

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Interactive Discussion

Discussion Paper

tions with climatological observations (of methyl nitrate) from aircraft and ground based measurement platforms highlight that the inclusion of the laboratory data for the title reaction from Butkovskaya et al. (2012) (simulation HIGBR) leads to levels of methyl nitrate which are too high to support use of the branching ratio of 1%. Further simulations adopting a lower limit of the branching ratio, similar to that recommended by Tyndall et al., (2001), (LOWBR) results in levels of methyl nitrate which are, generally speaking, within the range of observed values. The simulation that gives rise to the best agreement with the observations adopts this lower limit branching ratio reported by Butkovskaya et al. in combination with primary emissions of methyl nitrate and higher alkyl nitrates from the oceans (modified after Neu et al (2008)). Generally speaking, this is a topical study and one that helps to provide some guidance to other modeling groups (and laboratory groups) on the impacts of the laboratory study of Butkovskaya et al., beyond what can be deduced with a back of an envelope calculation. The authors demonstrate, clearly, that the results using the upper limit determined in the Butkovskaya et al. study are irreconcilable with our current understanding of the amount and distribution of methyl nitrate in the atmosphere, and its loss mechanisms. I feel that these model sensitivity studies are a useful addition to the literature and as such I would recommend publication of the paper after the authors address the following comments.

Specific comments: Missing sources of methyl nitrate. The authors come to the conclusion that there are missing sources of methyl nitrate. Flocke et al. (1998a) and Archibald et al. (2007), have shown that the reaction: CH3O + NO2 -> CH3ONO2 Can be a significant source of methyl nitrate under conditions of high NO2 (the polluted boundary layer and the lower stratosphere). Have the authors considered this source?

20112 – line 17. I suggest you remove the “improves when” and add “upon”.

20116 – line 24. I think the sentence may need a bit of re-working/tweaking.

20117 – line 6. The “on” at the end of the line should be “in”.

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20120 – line 14. Where is the reference for Flocke et al. 2008?! This is something that should have been picked up before the paper was circulated for review (if not by the authors than by the publishers). See further comments below.

20122 – line 17. I suggest you define “hly” or replace with “hourly”.

20128 – line 9. Correct “potolysic”.

20129 – line 24. Could the reason for the steepness of the gradient be linked to the fact that the tropical middle troposphere is the region that dominates the loss of methyl nitrate (i.e. greatest photolysis flux)?

20130 – line 4. Correct the double “the”.

20130 – line 18. It is stated that the value of the branching ratio used for R10 is from Flocke et al., 1998a and takes the value of 4.5E-3 i.e. 0.45% (greater than the lower limit from Butska). Can the authors please clarify (i) the value of the branching ratio used in the FLIGHT scenario (ii) its origin. As it stands I am unclear on both. For example, in Flocke et al. (1998a) they determine a series of branching ratios of 5-10E-5 for stratospheric conditions and 1.5-3E-4 for tropospheric conditions.

20130 – line 25. Correct “thr”.

20132 – line 3. Correct the hanging comma.

20132 – line 28. Correct “Hpa”.

20140 – line 32. Correct “prodcution”.

Figure 2. Superscript needed for text describing color scale.

Figure 4. I would suggest looking into splitting the y axis so that for the instances where the model significantly overestimates methyl nitrate, the observations can be seen (else what’s the point of plotting them?). Or I would suggest that you scale the model fields (or observations) to give the same effect. What about also looking at the

diurnal cycle in the observed and modeled methyl nitrate? How does that differ? By the looks of it, the HIGHBR scenario shows a very pronounced diurnal cycle that is not seen in the observations. This is an important further line of evidence to reject the use of the 1% branching ratio.

Figure 6. The figure caption states that the dark blue data represents the results from P_T_pt03, whilst the figure legend suggest the dark blue data are from LOWBR. Please correct.

Figure 7. Correct the figure caption (i.e. is EMISS or EMISSDD data shown? In any case the data plotted is not orange).

Table 2: The text describing the FLIGHT simulation is misleading/wrong. In the body text in section 2.2 FLIGHT is referred to as being based on EMISSPT but having a BR of 0.045%, whereas in Table 2 FLIGHT is referred to as being based on LOWBR. Please correct. Also, I think it would help the reader if you add a column or a reference to the total emission flux going into the model for each scenario in Table 2.

References:

Archibald, A.T., et al. "Comment on: Long-term atmospheric measurements of C1-C5 alkyl nitrates in the Pearl River Delta region of southeast China by Simpson et al." Atmospheric environment 41.34 (2007): 7369-7372.

Butkovskaya, N. I., Kukui, A., and Le Bras, G.: Pressure and temperature dependence of methyl nitrate formation in the CH3O2 + NO reaction, J. Phys. Chem. A, 116, 5972–5980, doi:10.1021/jp210710d, 2012.

Flocke, F., Atlas, E., Madronich, S., Schauffler, S. M., Aikin, K., Margitan, J. J., and Bui, T. P.: Observations of methyl nitrate in the lower stratosphere during STRAT: Implications for gas phase production mechanisms, Geophys. Res. Lett., 25, 1891–1894, 1998a.

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Tyndall, G. S., R. A. Cox, C. Granier, R. Lesclaux, G. K. Moortgat, M. J. Pilling, A. R. Ravishankara and T. J. Wallington, 2001, J. Geophys. Res., 106, 12157-12182.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 20111, 2013.