Atmos. Chem. Phys. Discuss., 13, C7430–C7436, 2013
www.atmos-chem-phys-discuss.net/13/C7430/2013/
© Author(s) 2013. This work is distributed under
the Creative Commons Attribute 3.0 License.

Atmospheric Chemistry and Physics Discussions

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 #2

Received and published: 27 September 2013

In "The impact of the chemical production of methyl nitrate from the NO + CH3O2 reaction on the global distributions of alkyl nitrates, nitrogen oxides and tropospheric ozone: a global modeling study," the authors attempt to reconcile recent laboratory measurements of CH3ONO2 formation, yet to be independently verified, by implementing the reaction in a 3D global CTM (TM5) and comparing with a global dataset of CH3ONO2 measurements. Due to the importance of this reaction on the oxidative capacity of

the atmosphere (i.e. O3 and OH) and the richness of the CH3ONO2 datasets, this approach is reasonable and worthwhile.

Comparing a series of sensitivity simulations to observations, the authors show that the recently reported literature value of CH3ONO2 formation rate (Butkovskaya et al 2012) is highly unlikely given our knowledge of other sources and sinks and the observations of CH3ONO2. In addition to answering this overarching question, the authors investigate the sensitivity of O3 production and global OH concentrations to various assumptions.

While there are important contributions in this manuscript, the message can be much more clearly conveyed. I found that the analysis of the CH3ONO2 formation rate to be lacking, specifically with regards to the vertical and temporal variability of CH3ONO2 and the lack of the HIPPO dataset. Furthermore, I found that the discussion of higher order alkyl nitrates and NOy to be beyond the scope of this current work and to be a distraction.

This manuscript can be improved with changes to both the content and the style. I suggest 1) moving a detailed discussion of the CH3ONO2 budget and uncertainties earlier in the manuscript, 2) better organization, particularly of the naming and ordering of the sensitivity studies in the manuscripts, and improved precision of scientific language, 3) limiting the number of issues discussed, 4) inclusion of additional datasets (HIPPO), and 5) discussion of the discrepancy between model and observations in the vertical (e.g., Fig. 6)

Below, I provide more detail on the above suggestions and provide some examples from the manuscript.

1) To provide context to the entire study, I suggest the authors present an annually-averaged, globally-integrated budget of CH3ONO2 early in the manuscript. Topics to address could include the following a. What is known about the day-to-day and regional variability of oceanic biogenic CH3ONO2 emissions? Do any of the cited papers pro-

vide an estimate of the uncertainty, the variability? b. The same questions with regards to deposition. c. What is the global annual average concentration observed at all of the ground sites and what is simulated in each of the scenarios?

2) In general, the organization of the experimental setup (the series of simulations), the paragraphs describing the observations, and figures are challenging to follow. More detailed comments are given in the minor comments below.

Since the authors refer often to the sensitivity simulations, it would be helpful to reconsider the naming scheme (E.g., using names like EMISS, EMISSDD and DEMISS and EMISSPT to assess chemical production is confusing). Also, maintain consistency within the figures, and clear figure headings (e.g., difference of EMISSPT and EMISS in Fig. 1 and and difference of BASE and EMISSPT in Fig. 2). Is the BASE simulation necessary for this analysis? Or should EMISS be the BASE simulation.

3) To narrow the focus, I suggest removing analysis of the CARABIC dataset. The NOy measurements have a stated uncertainty of 8%, alkyl nitrates only make up approximately 10% of NOy on average, and CH3ONO2 are only a small fraction of that. Since it is important that the model is reasonable with regards to NOy, I suggest the authors include a sentence like "the model has been compared to NOY datasets, including measuremnts from the CARABIC campaign and found to have reasonable agreement with. . .. "

I also suggest dropping discussion of higher order alkyl nitrates and associated figures and tables (Fig 3, Table 4, Fig 7). The ideas added by these figures can be summarized in a sentence or two to maintain narrow focus on CH3ONO2, O3, OH and NOx. Also, I presume that the behavior of species XO2N is not widely known by the larger atmospheric chemistry community, and thus should be avoided (E.g., Table 4).

4) For the observations used, please include a figure with three or four map panels that show the simulated annual-average CH3ONO2 with standard emissions and 1%, 0.3% and Flocke et al., 1998 branching ratios and some indication of surface measurements

(i.e. colored scatter plots for average observed values). As an alternative to this suggestion, include the nearest city, country, or air basin for each dataset as well as the corresponding simulated values for different branching ratios in Tables 1a,b.

Since this manuscript is largely focused on the relative importance of oceanic and chemical sources of CH3ONO2, it would be nice to see an analysis of the regional or day-to-day variability in a region where one would expect the variability to be controlled by each source. Furthermore, I would suspect that the CO signature of each source category would be quite different (and easy to show with the models), and could be used to better constrain the relative size of each source.

Consider including the HIPPO dataset in the analysis. After downloading the data and sorting, there are 1160 reported values for MeONO2. The measuremnts span the Central Pacific from approximately 80 degree S to 80 degree N and the full troposphere. The dataset could be useful for constraining the source of CH3ONO2 due to its latitudinal coverage. For example, in Figure 1, the authors show that the meridional gradient over the Central Pacific is very sensitive to MeONO2 formation rate (for 0.3% branching ratio, 0 -10 ppt at Equator and Antarctic, 10-20 ppt at S midlatitudes and 30-40 ppt in the N midlatitudes), a region covered by HIPPO.

5) Please discuss the large discrepancy between the observed and simulated vertical profile of CH3ONO2 in more detail (i.e. Fig 6). There appears a to be a consistent increase of CH3ONO2 from 8 km to 10 km. The authors state that the discrepancy is instead due to transport (P20129, L29), which I find unlikely. It appears that the models that include chemical production of CH3ONO2 simulate a similar feature albeit at much smaller magnitude while emissions only sources have nothing like it. Do the authors know of any possible temperature or pressure dependent source? Do they know of any that have been hypothesized? Is it possible that the CH3O2 + NO reaction rate has a strong temperature dependence? Please discuss in more detail.

Please also consider the following comments. Abstract) Edit to fit with changes made

to manuscript. Please give some estimate of the range of branching ratios that seem possible given the observed values

20113 - L6) What about CO?

20113 – L20) Awkward discussion of O3-NO2-NO steady-state. NO + O3 is a fast in many locations, and slower at high NOx (O3 titrated to 0).

20114 – L 6) "long-lived nitrogen reservoirs" to oxidized nitrogen species or NOy, PAN and some AN's are not long-lived

20114 – L 11) Please use more standard terminology for alkyl nitrates (i.e., RONO2)

20114 – L 14) Awkward conversation of radical chemistry. Maybe only discuss HOx-NOx chain terminating reactions in previous paragraph and drop this paragraph. HOx-HOx reactions dominate the global budget.

20114 – L 14) In this instance maybe should be "may be"; correct through out manuscript please.

20115 – L28) Possibly mention different methods typically used to measure ANs, differences between specific and sum ANs (i.e., TD-LIF)

20116 – L13) Change "nitrogen reservoirs" to "reactive N"

20116 – L13) delete "direct" "additional" "without the need of long range transport"

20116 – L20-25) Do any of these studies provide estimates of the variability or uncertainty of these processes at a global scale. I.e., does that range justify the range of sensitivity simulations used in this work.

20118) Write out ODIN, UARS

20118 – L25) Add "Further updates to the model used in this study include"

20119 – L17) correct "described Williams"

20120 – L25-) Should this description be moved to section 2.1 Model description

20121) Possibly shorten description of each measurement site and provide references for those interested in more detail

20122 – L17) Hourly not hly.

20123 – L18) use "simulated" instead of "shown"

20124 – L13) Yes CH3ONO2 has a higher solubility than higher ANs, but that does not mean it has a higher solubility than PAN, the value adopted. I would prefer to see some mention of the range of possible values for similar compounds to gauge the uncertainty in the deposition rate.

20124 – L23-28) Awkward. consider revising.

20125 and throughout) consider using global average ppt as units instead of burden. Budget terms in Tg/ yr is good though.

20126 – L19) add simulated to "shows the daily variability" I think Fig 4 would be improved by scaling the data or using a y-log scale. Also, it is also unclear to me whether this data shows any measurements. Please clearly distinguish measurements from simulated values.

20128- L5) Check values with Table and earlier mention of same site.

20129 – L14) Please discuss whether this variability is useful to differentiate oceanic and chemical sources, if not in the observations, than in a model.

20130 – L18) Please use consistent percent units for the braching ratio. Is this 0.0045%?

20131 – 20134) Much of this seems beyond the scope of this work and could be summarized in a sentence or two.

Tables: (See major comments above) – The names of the model simulations confused

me throughout, please consider changing. Also, location names in Table 1 would be useful.

Table 5 Figures : In general, use different color scales for difference plots and include some header that describes what the plot is showing (e.g., Fig 1. ECH3ONO2-only and impact of PCH3ONO2)

I found Figs 3, 7 and 8 to be beyond the scope of this paper. Also, Fig. 7 is where some of my confusion about ORGNTR occurred. Is ORGNTR all RONO2 or is it just C-1-5 compounds?

Fig 2- This figure may be unnecessary (the description of deposition in the text seems sufficient). But if you keep, please use units that are useful to compare with budget terms.

Fig 4 : The observed values (short green lines?) are very difficult to see.

Fig 5+6: Good figures. I think figure 6 is useful for the manuscripts “take-home” message.

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