**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Global and regional effects of the photochemistry of CH$_3$O$_2$NO$_2$: evidence from ARCTAS" *by* E. C. Browne et al.

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We thank the referees for their helpful comments and suggestions and will address the comments in a revised manuscript. Here we respond to the comments from the reviewers.

Responses to Anonymous Referee #1

Referee: Is there a consistency between the indirect measurements of CH3O2NO2 during ARCTAS and the photochemical calculations? It would be useful to show a direct comparison of those two quantities. It may be that the uncertainties associated with both result in a poor point to point comparison which doesn't necessarily render the broader (bulk) comparison invalid. (Second comment) It was pointed out to me

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that my first comment is not clear (re: comparing inferred values with model). I was referring to a point-by-point comparison with GEOS-Chem calculations. It indeed may not be useful, given the uncertainties driven by the varying precursor fields...just a curiosity question.

Response: We agree that this would be an interesting comparison. However, in our GEOS-CHEM modeling our objective was to examine how inclusion of methyl peroxy nitrate chemistry affects atmospheric composition on a regional and global scale. We did not attempt to directly simulate the ARCTAS conditions which included unusually early biomass burning in eastern Siberia (Jacob et al., 2010). Our GEOS-CHEM run uses monthly mean GFED2 biomass burning emissions from 2006. Therefore, we feel that a point-by-point comparison would tell us more about interannual differences in emissions and transport than it would about the model's ability to predict the airplane observations.

Referee: p. 2242 discussion 1st paragraph and Figure 1: this analysis does not include the coldest temperatures measured during ARCTAS. I note that the filtering to restrict the analysis to ARCTAS data where $CH_3O_2NO_2$ lifetimes are less than 12 hours should in effect remove the majority of the data at the highest altitudes and at the coldest temperatures. (I suspect that upper tropospheric values could be possibly even higher than the 10-20 ppt range, depending on the availability of radicals at the cold higher altitudes). This statement needs to reflect that the coldest temperatures are not included in this analysis. The filtering is also reflected in Figure 3 (discussion in section 4.1), and is the likely reason that the line for ARCTAS observations does not span the temperature or concentration ranges for the GEOS-Chem spring season.

Response: Yes, this is correct. We enacted these strict filtering requirements to ensure that our photostationary state assumption is applicable. If we apply a less stringent filter, we calculate $CH_3O_2NO_2$ concentrations of ∼20-90 pptv at 220 K. However, we take a conservative approach and only report results where we are confident that the assumptions of our photostationary state are valid. We have added the following sen-

tence into section 3 (pg 2240, line 19) to clarify this: These restrictions exclude measurements from the coldest temperatures/highest altitudes sampled during ARCTAS: conditions under which we would expect high concentrations of CH3O2NO2.

We have also revised the first sentence on pg 2242 to clarify this (lines 3-4): ...values of up to ∼5-15 pptv in the coldest conditions sampled during ARCTAS that satisfy our photostationary state criteria (Fig. 1). It is probable that larger concentrations of CH3O2NO2 were present during ARCTAS in conditions under which our photostationary state assumption fails.

In section 4.1 (page 2243 line 11) we have added the following to address the difference our filtering may cause in the comparison to the GEOS-CHEM results: The spring (March, April, May) concentrations are slightly higher than the concentrations inferred from the ARCTAS observations of XNO2 (Sect. 3). We expect that part of this discrepancy is due to exclusion of non-photostationary state conditions from the ARCTAS observations.

Referee: Abstract: Concentrations of CH3O2NO2 are listed as 5-15 ppt here, and 10-20 ppt in the discussion p. 2242 1st paragraph. These should be consistent.

Response: Yes. We have changed the concentrations in the discussion (pg 2242 line 2) to 5-15 pptv.

Referee: p. 2245 Implications: Re: discussion of the INTEX-NA results from Ren et al. First, the box model used in Ren et al. includes CH3O2NO2; however impacts due to including vs. not-including that chemistry in box models of this type are limited because they are constrained to observed NOx. Therefore in this case, the measurement/model discrepancies in Ren et al. shouldn't be described as consistent with the chemistry of CH3O2NO2. However it is quite valid (and important), as the authors note, that if the measurements of NO2 are in fact XNO2 the modeled HO2/OH could be erroneously high. It would be very interesting to see the same type of analysis on the INTEXNA data as was done for ARCTAS. If the authors can show that an overestimate in measured

NO2 contributes significantly to the HO2 model/measured discrepancy, that would be extremely compelling.

Response: Thank you for these comments. We were unaware that the box model in Ren et al. (2008) included CH3O2NO2 chemistry. We agree that an analysis of the INTEX-NA data would be extremely informative; however this analysis is outside the scope of this paper. Upper tropospheric measurements of INTEX-NA were strongly influenced by recent convention which precludes a photostationary state analysis of the data. A detailed analysis of the influence of CH3O2NO2 chemistry would necessitate a more comprehensive model that would account for the NOx and HOx precursors that are out of steady-state. However, we feel that it is important to discuss how CH3O2NO2 chemistry alters upper tropospheric HO2 and OH and have changed the paragraph (pg 2245 line 14-26) to read: The decrease in upper tropospheric NOx from inclusion of CH3O2NO2 results in increases in HO2 and decreases in OH in the upper troposphere, thus increasing the HO2 to OH ratio. During the Intercontinental Chemical Transport Experiment-A (INTEX-A) Ren et al. (2008) found that the observed HO2/OH ratio was larger than box-model predictions in the upper troposphere. Although the box-model used in Ren et al. (2008) contains CH3O2NO2 chemistry, it was constrained to measured NO2 concentrations. It is likely that these concentrations are measurements of XNO2. We expect that the difference in the box model results constrained to XNO2 versus the results constrained to NO2 would be qualitatively similar to the changes observed between our base case and MPN case GEOS-CHEM runs. The magnitude of the change in HO2 between the MPN and base case runs is significantly smaller than the measurement-model differences observed during INTEX-A by Ren et al. (2008). We conclude that CH3O2NO2 interference in the NO2 measurement during INTEX-NA may be responsible for part of the difference between measured and modeled HOx and NOx during INTEX-NA, but there are still unexplained measurement-model discrepancies.

Referee: Section 4.1 line 20 – discussion of why HO2NO2 and N2O5 are higher in

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the arctic fall and winter when CH3O2NO2 chemistry is included in the model. I don't follow the explanation given. Could part of the issue be due to differences in HO2/OH and NO2/NO partitioning with the addition of the chemistry?

Response: The increases observed in N2O5 and HO2NO2 between temperatures ~240 K to ~255 K are due to an increase in chemical production caused by an increase in NO2 concentrations in these temperature regions in the MPN case as compared to the base case. This increase in NO2 is presumably due to thermal dissociation of CH3O2NO2 that has been transported from colder regions. It should be noted that these represent small absolute changes. In order to explain this more clearly, we have revised p.2243 lines 20-25 to read: These increases result from an increase in chemical production of N2O5 and HO2NO2 in the MPN case relative to the base case. The increase in chemical production is due to increased NO2 concentrations (at 240 K NO2 is 20% larger in the winter and 16% larger in fall). This increase in NO2 is presumably due to thermal dissociation of CH3O2NO2. It should be noted that although these are large relative changes, they represent absolute changes of generally less than 1 pptv.

Referee: I am very surprised at the dramatic response of CH3OOH to the addition of this chemistry. Figure 4f shows the summer increase at 220K is _14%. Photolysis loss to CH3OOH should be approximately equivalent to that from OH, so I am skeptical that a change in lifetime due to decreases in OH can be the primary cause. As its production is due to reaction of HO2 and CH3O2, it would be interesting to see the response of those radicals. Although HO2 increases, it seems unlikely or at least surprising that its increase is enough to explain the 14% larger value of CH3OOH. Even more dramatic is the 30-75% increase in CH3OOH in the tropical biomass burning plumes, where the equivalent HO2 increases are shown as 10-25% - is the change in HO2/OH ratio really enough to explain up to a 75% CH3OOH increase? What does CH3O2 do? I would imagine that as OH decreases, CH3O2 would as well, which would buffer any increase in HO2. I think a more thorough budget explanation is necessary here.

Response: Our intent in this paper is to provide a brief overview of how the inclusion

of CH3O2NO2 chemistry alters tropospheric composition due to its role as a reservoir of CH3O2 and NO2. Since changing CH3O2 and NO2 concentrations alters the highly non-linear process coupling HOx and NOx and their reservoirs, a complete budget analysis of all the species is outside the scope of this paper. We clarify that we are not attempting a complete budget analysis on all these species by the addition of these sentences to p. 2242 line 25: We analyze output for January-December 2008. Twenty-four hour averaged concentrations are saved for both the first and second half of each month. In this analysis we focus on the resulting changes in tropospheric concentrations to NOx, ozone, N2O5, HO2NO2, HNO3, and methyl hydrogen peroxide. We choose these species as examples to illustrate that due to the highly coupled, non-linear relationship between NOx and HOx, altering NOx concentrations by including CH3O2NO2 chemistry changes: the cycling of NOx (and thus ozone concentrations), both short (N2O5, HO2NO2) and long-term (HNO3) NOx reservoirs and sinks, and HOx reservoirs (CH3OOH). We do not attempt a thorough budget analysis of the changes in all of these species; our goal is to illustrate how changes resulting from inclusion of CH3O2NO2 chemistry affect tropospheric composition.

Additionally, we have expanded on our description of the causes of CH3OOH changes. In section 4.1 (North American Arctic) we have revised the section on methyl hydrogen peroxide to read (p. 2244 line 1-5): The HOy species methyl hydrogen peroxide shows increases of up to ∼14% (∼3 pptv) at ∼220 K in the summertime (Fig. 4f). Smaller increases occur at other times of year. The changes in methyl hydrogen peroxide concentrations are due to increases in chemical production (resulting from higher HO2 concentrations), increases in lifetime due to the lower OH concentrations, and changes in the concentrations transported into the region. At 220 K, chemical production is increased ∼4% in the MPN case relative to the base case in the spring and in the summer it is increased by ∼10%. The lifetime of methyl hydrogen peroxide in the MPN case relative to the base case increases by ∼6% in the spring and ∼9% in the summer.

We have added the following discussion regarding methyl hydrogen peroxide to the

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discussion regarding the tropics (p. 2244 line 26): As in the arctic, changes in methyl hydrogen peroxide are due to a combination of increased chemical production and increased lifetime in the MPN case compared to the base case. In the biomass burning plumes chemical production is up to ∼90% faster in the MPN case and the lifetime is ∼29% longer.

Responses to Anonymous Referee #2

Referee: The only aspect of the paper that I would like the authors to revisit and per-haps expand is the steady state modeling. While my suggestion may not make a large difference to the conclusions of this modeling (such as those in Fig. 2), it seems that some important reactions have not been included. I take it that the primary produc-tion of OH from ozone photolysis in the UV-B is not necessary because the model is constrained by observed OH and HO2. If so, this should be stated. An alternative approach would be to let OH and HO2 also be calculated, and to assess the degree of agreement between the measurements and the model values (perhaps beyond the scope of this paper, but also a partial test of the mechanism). Perhaps that is also why other HOx sources such as CH2O, H2O2, and HO2NO2 photolysis were omit-ted. Maybe this entire issue can be addressed with a sentence or two in the model description.

Response: We constrained the model using measured HO2 and OH. We agree that it would be interesting to calculate OH and HO2; however, considering that our photo-stationary state model is trying to decouple NO2 and CH3O2NO2 from the measured XNO2, we feel that constraining the model to measured values whenever possible re-duces the uncertainty in our determination of CH3O2NO2 and NO2. To make it clear that we constrain the model to measured OH and HO2, we have changed section 3 (p. 2240 lines 22-23) to: . . .concentrations of species listed in Table 1 were used to constrain the model. The use of the measured OH and HO2 concentrations enables us to exclude HOx source reactions from our photostationary state model.

Referee: Have you performed laboratory experiments with a methyl peroxynitrate source and varying inlet sample times to address the impacts of uncertainties in the instrument residence time on the calculations mentioned in line 8, page 2241?

Response: We have not conducted these experiments. The residence time of our instrument was determined by varying the inlet and outlet pressures to simulate aircraft conditions and then measuring the flows. The uncertainties in the residence time reflect the difficulty in simulating aircraft operating conditions in the laboratory. Due to the extreme thermal instability of $CH_3O_2NO_2$, any laboratory tests of its dissociation in the instrument at upper tropospherically relevant conditions would be subject to both the uncertainties in simulating the upper troposphere in lab and in the $CH_3O_2NO_2$ source.

We have added the following sentence to p. 2241 line 22 to clarify how the uncertainty was determined: The residence time in the UC Berkeley LIF was determined in the laboratory after ARCTAS was completed by varying inlet and outlet pressures to simulate aircraft conditions and measuring the flows. Due to the difficulties in simulating aircraft conditions in the lab, we assign an uncertainty of $\pm 25\%$ to our residence time.

Referee: On page 2241, there are a mixture of the plus/minus symbol and the keyboard version: +/-.

Response: The keyboard version is used because it is -/+ rather than +/- for these instances. To clarify this we have changed the last section of p 2241 to read: An increase of 25% in the residence time leads to decreases of approximately 10% in both NO_2 and $CH_3O_2NO_2$ concentrations at 230-235 K. A decrease in residence time of 25% results in $\sim$10% increases of NO_2 and $CH_3O_2NO_2$ in the same temperature range. A decrease in residence time results in an increase in both NO_2 and $CH_3O_2NO_2$ because the decreased residence time results in smaller fractions of $CH_3O_2NO_2$ and HO_2NO_2 that dissociate in the inlet. Since we force the sum of dissociated $CH_3O_2NO_2$, dissociated HO_2NO_2, and calculated NO_2 to equal the measured XNO_2, the decrease in the fractions of $CH_3O_2NO_2$ and HO_2NO_2 that dissociate results in a larger concentration

of NO2 and thus a higher calculated steady state CH3O2NO2.

Referee: On page 2246, line 18, I think you mean ": : :in the inlet of NO2 instruments: : :" rather than ": : : NO2 measurements: : :".

Response: Yes, that is what we mean. We have changed measurements to instruments.

Referee: It is the authors' choice, but personally I prefer symbols with error bars for binned values such as in Figs. 1 and 3. They show the range of values and bin width clearly.

Response: We thank the referee for this suggestion. We feel Fig. 1 is well represented using the symbols and the line representing the median values. We have made Fig. 3 as per your suggestion, but there is substantial overlap in the error bars for each season, making the figure difficult to read. We have amended the caption of Fig. 3 to make it clear that we are only plotting the temperature binned, mean value. The caption now reads: Temperature binned mean values of the GEOS-CHEM modeled CH3O2NO2 concentrations over the North American Arctic as a function of temperature and season.

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