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Interactive comment on “Global and regional effects of the photochemistry of $CH_3O_2NO_2$: evidence from ARCTAS” *by* E. C. Browne et al.

Anonymous Referee #1

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Comments on global and regional effects of the photochemistry of CH3O2NO2: evidence from ARCTAS by Browne et al.

This paper examines the impact of methyl peroxy nitrate on tropospheric chemistry, using indirect measurements during ARCTAS and a steady state modeling approximation, and then using the global model GEOS-Chem. It is quite brief and cursory, but I think it raises a very interesting issue and makes a good quick first-approach analysis of the impact of this compound on global/regional tropospheric chemistry. I have identified a few points that I think deserve more attention and clarification. I wonder if a more appropriate venue might be GRL. Given a decision that ACP is appropriate, I would recommend publication after minor revision.

Analysis of ARCTAS data: 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.

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 CH3O2NO2 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.

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.

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 INTEX-NA 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.

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

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 $\sim$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.

This paper is quite short and doesn't go into great detail (more of a GRL type paper?) but leave a decision as to its appropriateness for ACP to the editor.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 2233, 2011.