

## ***Interactive comment on* “Global and regional effects of the photochemistry of CH<sub>3</sub>O<sub>2</sub>NO<sub>2</sub>: 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 CH<sub>3</sub>O<sub>2</sub>NO<sub>2</sub>: 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

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of  $\text{CH}_3\text{O}_2\text{NO}_2$  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  $\text{CH}_3\text{O}_2\text{NO}_2$  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.

Abstract: Concentrations of  $\text{CH}_3\text{O}_2\text{NO}_2$  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  $\text{CH}_3\text{O}_2\text{NO}_2$ ; however impacts due to including vs. not-including that chemistry in box models of this type are limited because they are constrained to observed  $\text{NO}_x$ . Therefore in this case, the measurement/model discrepancies in Ren et al. shouldn't be described as consistent with the chemistry of  $\text{CH}_3\text{O}_2\text{NO}_2$ . However it is quite valid (and important), as the authors note, that if the measurements of  $\text{NO}_2$  are in fact  $\text{XNO}_2$  the modeled  $\text{HO}_2/\text{OH}$  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  $\text{NO}_2$  contributes significantly to the  $\text{HO}_2$  model/measured discrepancy, that would be extremely compelling.

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Section 4.1 line 20 – discussion of why HO<sub>2</sub>NO<sub>2</sub> and N<sub>2</sub>O<sub>5</sub> are higher in the arctic fall and winter when CH<sub>3</sub>O<sub>2</sub>NO<sub>2</sub> chemistry is included in the model. I don't follow the explanation given. Could part of the issue be due to differences in HO<sub>2</sub>/OH and NO<sub>2</sub>/NO partitioning with the addition of the chemistry?

I am very surprised at the dramatic response of CH<sub>3</sub>OOH to the addition of this chemistry. Figure 4f shows the summer increase at 220K is ~14%. Photolysis loss to CH<sub>3</sub>OOH 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 HO<sub>2</sub> and CH<sub>3</sub>O<sub>2</sub>, it would be interesting to see the response of those radicals. Although HO<sub>2</sub> increases, it seems unlikely or at least surprising that its increase is enough to explain the 14% larger value of CH<sub>3</sub>OOH. Even more dramatic is the 30-75% increase in CH<sub>3</sub>OOH in the tropical biomass burning plumes, where the equivalent HO<sub>2</sub> increases are shown as 10-25% - is the change in HO<sub>2</sub>/OH ratio really enough to explain up to a 75% CH<sub>3</sub>OOH increase? What does CH<sub>3</sub>O<sub>2</sub> do? I would imagine that as OH decreases, CH<sub>3</sub>O<sub>2</sub> would as well, which would buffer any increase in HO<sub>2</sub>. 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.

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

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