Response to Reviewer Document
Title: Atmospheric peroxyacetyl nitrate (PAN): a global budget and source attribution

We thank both reviewers for their thoughtful comments. We have incorporated the suggestions as indicated below. *Our responses are in italics*.

Reviewer 1:
GENERAL COMMENTS:

The manuscript discusses the global budget of PAN, an important reservoir for NOx in the troposphere and a chemical species central to tropospheric ozone production. An extensive source attribution for PAN is also included. The authors apply a typical modelling approach using a well established and tested 3D global chemistry-transport model (GEOS-Chem). In addition to deriving the PAN budget and identifying and quantifying the major sources of PAN the work includes further innovation in two ways: 1) by improving the GEOS-Chem representation of the chemistry of PAN and its precursors synthesizing recent advancement into the model and 2) by creating a new comprehensive database of PAN observational data for model evaluation. The global PAN distribution in the GEOS-Chem model is evaluated against this newly created dataset.

While maybe not breaking ground on all fronts, in my opinion this paper represents a solid and most useful piece of science. It is well within the scope of ACP, overall well written and presented and is positively worth publishing.

I believe there really isn't much to be criticised about this manuscript. Abstract and introduction are useful, existing literature is comprehensively cited and the results are presented and discussed clearly and logically. Tables and figures are prepared and used well, are meaningful and are helpful in discussing the science. The conclusions are concise and down to the point. The language is clear and the thread is (mostly) consistent.

I do not always agree with the choice of figures selected for the main text and the supplement (see specific comments) but I appreciate that it is sometimes difficult to bring down the large amount of visual data to the size of a meaningful manuscript. At times the discussion strays away from the specific result being discussed extending onto closely (and not so closely) related results but always remains topical and factual.

Yes, it was difficult to incorporate a large amount of visual analysis into a reasonable number of figures for the paper. This may also explain the impression that the discussion includes more information than expected in certain sections. This has been improved in response to the specific comments where possible (see below).

It is debateable whether this is only a question of writing style or may be considered a more serious weakness; in any case, I do not believe it diminishes the manuscript in any significant way.

SPECIFIC COMMENTS

p. 26,851; l. 5-7: The paper states that the "finer horizontal resolution [in the GEOSChem sensitivity experiment] produces 10-20% more PAN". Unfortunately, this finding is not explored any further. It would be interesting to know to what process the increased PAN production is owed (better resolution of (pyro)convection, more accurate distribution of fire emissions, etc.).

We added the following to the text:
"The likely explanation is that vertical transport is faster at higher resolution because eddies are not averaged out. This was first shown by Wang et al. (2004) using a nested simulation for CO over Asia."

Further Discussion:
More recently, Zhang et al. (2011) also found that a higher resolution nested model produced higher surface ozone in the intermountain West. This sentence in the paper is based on a comparison of PAN concentrations produced at a horizontal resolution of 4°x5° versus 2°x2.5°. When the 2°x2.5° output is averaged to the 4°x5° grid, the most pronounced difference appears to be for northern Eurasian fires in spring. The difference is largest near the surface (10-20%), but is generally less than 5% above 1 km. There are differences in the concentrations of many other species, including NO_x, particularly at the surface between the two resolutions. Another potential issue is that OH is a function of resolution [see Charlton-Perez et al., ACP 2009 for example]. We did explore this issue beyond what is presented in the paper by comparing output from the model presented in Ellis et al., [2013]. This output did not have the PAN updates included as described here. However, we compared the PAN in their nested simulation over North America during July to that produced by the global simulation with 2°x2.5° resolution. There were also differences in PAN between these two resolutions, with the finer resolution again producing more PAN. Here the difference was larger over the middle of the U.S. – not in fire regions, thus there may be more than one reason for discrepancies due to resolution and the differences may vary depending on the resolutions that are compared.

References for this Discussion:

Charlton-Perez, C. L., Evans, M. J., Marsham, J. H., and Esler, J. G.: The impact of resolution on ship plume simulations with NO_x chemistry, Atmos. Chem. Phys., 9, 7505-7518, doi:10.5194/acp-9-7505-2009, 2009.

Ellis, R. A., D. J. Jacob, M. P. Sulprizio, L. Zhang, C. D. Holmes, B. A. Schichtel, T. Blett, E. Porter, L. H. Pardo, and J. A. Lynch (2013), Present and future nitrogen deposition to national parks in the United States: critical load exceedances, Atmos. Chem. Phys., 13(17), 9083-9095, 10.5194/acp-13-9083-2013.

Wang, Y. X., M. B. McElroy, D. J. Jacob, and R. M. Yantosca (2004), A nested grid formulation for chemical transport over Asia: Applications to CO, Journal of Geophysical Research: Atmospheres, 109(D22), D22307, 10.1029/2004JD005237.

Zhang, L., D. J. Jacob, N. V. Downey, D. A. Wood, D. Blewitt, C. C. Carouge, A. van Donkelaar, D. B. A. Jones, L. T. Murray, and Y. Wang (2011), Improved estimate of the policy-relevant background ozone in the United States using the GEOS-Chem global model with 1/2° × 2/3° horizontal resolution over North America, Atmospheric Environment, 45(37), 6769-6776, http://dx.doi.org/10.1016/j.atmosenv.2011.07.054.

p. 26,854; l. 15 ff.: Should figures from the supplement be made an integral part of the main text? In other words, why not move the figure from the supplement to the main text when it is discussed there, anyway. Either include the figure in the main text or remove the discussion from the manuscript. The reader should not feel it necessary to turn to the supplement in order to follow the main line of discussion.

We have removed the reference to the supplemental figures as suggested.

p. 26,855; l. 5: It would be helpful, I think, to point out that the austral-Spring features discussed in Figure 2 correspond to the SON seasonal mean plots.

We have added a reference to the SON seasonal mean plots to this sentence as suggested.

p. 26,856; l. 13: Again, if it is an important result/figure then it should be included in the main text rather than putting it in the supplement.

This information is all included in the main figures/tables and is not in the supplement. This comment might be pointing to an incorrect line number. We did remove all references to S1 and S2 in the main text as suggested above. These figures are mainly included in the supplemental material so that model comparisons for specific field missions /regions, which we expect to be of interest to the experimental community, can be easily found.

p. 26,856; l. 8 ff.: Usually, by applying an annihilation perturbation one risks forcing the model into a non-linear response (as is, indeed, argued a few lines below in connection with the isoprene sensitivity scenario). I have two related questions to this: 1) why has the annihilation perturbation scenario been chosen for most of the sensitivity experiments (e.g., to increase the signal-to-noise ratio perhaps) and 2) has there been made an attempt to analyse whether the response in these annihilation perturbation experiments are non-linear (e.g., by repeating one of these experiments with a 20% perturbation and then up-scaling the response to 100%; a comparison between this and the annihilation experiment should reveal non-linearities).

As pointed out by the reviewer, we realize that nonlinearities exist. This is also discussed in reference to Figure 4. Though they would increase the signal, the annihilation *perturbation scenarios for Table 1 were chosen mainly for logistical reasons. The sheer volume of model parameters that need to be changed to fully understand the nonlinearity for all the NMOVCs relevant to PAN, makes this operationally tedious within GEOS-Chem. (The emissions in model version v9.01.01 are controlled by various different modules.) It is also easier to verify with 100% certainty that the emissions have been turned off completely with annihilation experiments. As suggested, we performed a simulation with isoprene emissions turned completely off. This can be compared to the simulation with a 20% reduction (as in Table 1) to gain some insight into a model perturbation that we expect to produce highly nonlinear results. Here a 100% reduction (instead of an upscaled 20% reduction) changes the contribution of isoprene to PAN from 37% to 40%. Of course, each VOC could be different, but this suggests that our choice of annihilation experiments would not change the overall interpretation of Table 1.*

p. 26,860; l. 20: With the new chemistry mechanism in GEOS-Chem, which includes an OH-recycling mechanism, it would be interesting to quantify the impact of OH-recycling on PAN formation. This should be easily done by one further sensitivity experiment.

As requested we did an additional sensitivity simulation without the $HOCH_2C(OO)(CH_3)CH{=}CH_2$ *(RIO2 is GEOS-Chem species) isomerization reaction. We find that surface PAN over the Amazon is highly sensitive to OH-recycling (50%); however, this is a region of relatively low PAN concentrations in the model (<200 pptv monthly mean). OH recycling does impact the PAN distribution aloft (mid troposphere) over the Eastern US and NE Atlantic during summer. Here OH recycling reduces PAN over the continent and increases it over the Atlantic. The differences are on the order of 100 – 200 pptv. The upper troposphere austral spring features in the model are largely insensitive to OH-recycling. This also does not appear to impact the springtime PAN export from East Asia.*

p. 26,883; Table 1: I do not quite understand why the terpene lifetime is longer than that of isoprene; I would have thought that this generally was the other way round. Is this because of the lumped nature of the species?

Yes, this is the calculated lifetime within the model for the lumped species. We have added an additional few words to footnote 'g' in Table 1 to indicate this.

p. 26,889; Figure 5: I really like this figure and the way it presents the connection between PAN and its precursor species.

Thank you! This figure took many iterations!

SMALL STUFF AND TYPOS:

p. 26,846; l. 12: "both" –> "all"

Suggested change has been made.

p. 26,850; l. 3: ...directly to PAN and HNO3, respectively. (comma after HNO3).

Suggested change has been made.

p. 26,857; l. 18: remove one "that" from sentence.

Suggested change has been made.

I have checked the references against the citations in the text and found a few inconsistencies worthwhile checking:

"Beine et al., 2000" is in the references but does not seem to be cited in the text.

This reference is cited in Table 2.

"Bottenheim et al., 1994" is in the references but does not seem to be cited in the text.

This is cited on p 26,852, line 15.

"Lurmann et al., 1986" is in the references but does not seem to be cited in the text.

This is cited in a footnote in Table 1.

"Val Martin et al., 2008" is in the references but does not seem to be cited in the text.

This is cited on p 26,854, line 11.

"Worthy et al., 1994" is in the references but does not seem to be cited in the text.

This reference is cited in Table 2.