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 2:
GENERAL COMMENTS:

By including emissions of aromatics, tuning biomass-burning emissions of short lived VOCS and also the fraction of biomass burning air that directly penetrates the boundary layer, this study captures important features in the observational datasets for PAN. These tuning experiments provide insight into the major global sources of PAN and thus on its impact as a transporter of NOx and source of O3 in remote locations and also indicate where substantial uncertainties remain. The authors conclude (P28662, L17) that the work presented in their paper increases confidence in their ability to simulate the distribution of PAN within GEOS-Chem. However, given that the model was tuned to do exactly that, this is not really surprising.

Overall, this is an interesting and well-presented study and I have only minor comments, questions and suggestions for improvement, some of which are related to more transparent chemical schemes for formation of the PAN precursors.

General: PAN is properly named acetylperoxy nitric anhydride, not peroxyacetyl nitrate.

Yes this is always an issue with PAN. Is the historical name or the proper name a better choice? We recommend the use of peroxyactyl nitrate because acetylperoxy nitric anhydride is not in common use. Though this may risk irritating chemists, a name change will be confusing to atmospheric scientists. We have chosen to note the name issue in the text as follows:

"Peroxyacetic nitric anhydride ($CH_3COO_2NO_2$), commonly known by its misnomer peroxyacetyl nitrate (PAN), is the principal tropospheric reservoir species for nitrogen oxide radicals ($NO_x = NO + NO_2$) with important implications for the production of tropospheric ozone (O_3) and of the hydroxyl radical OH (the main atmospheric oxidant) (Singh and Hanst, 1981)."

P26845, L21. NO3 reactions with RO2 have been included and the reader is referred to Stone et al., a paper in discussion. Here, a short text about how these reactions were implicated would be appropriate. To what extent has the Stone et al. scheme been validated (the observations of HO2 and NO3 appear not to be well reproduced in their model). Do these reactions lead to radical regeneration?

Stone et al. (2013), which was in preparation at the time we submitted this manuscript, is now available on ACPD so we have focused the additional comments in our manuscript *on the implementation and its impact on PAN. We have added the following to the manuscript.*

"To implement the Stone et al., (2013) nighttime chemistry, we went through each of the RO_2 + NO reactions in the GEOS-Chem chemical mechanism, copied each of these reactions, and changed the RO_2 reactants to react with NO_3 rather than NO. The MCM considers three different reactions rates for this class, one for CH_3O_2, one for $RC(O)O_2$ and one for all other RO_2. There is no temperature dependence included and all products are assumed to be the same as the corresponding reaction of the RO_2 radical with NO (Bloss et al., 2005)."

Further discussion: We conducted simulations with and without RO_2 + NO_3 reactions to explore the extent to which PAN may be sensitive to poorly constrained nighttime chemistry. In short, the addition of RO_2 + NO_3 reactions increases PAN formation in the model, and the largest impact on simulated PAN mixing ratios coincides with the strongest PAN production (Eastern U.S. and East Asia). Here monthly mean surface PAN mixing ratios increase by ~50 pptv in spring and summer. The impact of nighttime NO_3 driven chemistry is more modest in the mid-latitude free troposphere. The addition of RO_2 + NO_3 reactions increases springtime PAN mixing ratios broadly over the Arctic by 5-10 pptv (~5%). The impact in summer is more heterogeneous at higher altitudes, but the overall increase is on the order of ~2% over most of the Arctic. We find that the addition of RO_2 + NO_3 chemistry increases O_3 over the Arctic during spring by ~0.5 ppbv at the surface, with larger increases aloft (~0.75 ppbv at 4 km)."

New References Added:
Bloss, C., Wagner, V., Jenkin, M. E., Volkamer, R., Bloss, W. J., Lee, J. D., Heard, D. E., Wirtz, K., Martin-Reviejo, M., Rea, G., Wenger, J. C., and Pilling, M. J.: Development of a detailed chemical mechanism (MCMv3.1) for the atmospheric oxidation of aromatic hydrocarbons, Atmos. Chem. Phys., 5, 641-664, doi:10.5194/acp-5-641-2005, 2005.
Stone, D., Evans, M. J., Walker, H. M., Ingham, T., Vaughan, S., Ouyang, B., Kennedy, O. J., McLeod, M. W., Jones, R. L., Hopkins, J., Punjabi, S., Lidster, R., Hamilton, J. F., Lee, J. D., Lewis, A. C., Carpenter, L. J., Forster, G., Oram, D. E., Reeves, C. E., Bauguitte, S., Morgan, W., Coe, H., Aruffo, E., Dari-Salisburgo, C., Giammaria, F., Di Carlo, P., and Heard, D. E.: Radical chemistry at night: comparisons between observed and modelled HO_x, NO_3 and N_2O_5 during the RONOCO project, Atmos. Chem. Phys. Discuss., 13, 9519-9566, doi:10.5194/acpd-13-9519-2013, 2013.

P26846, L26. The PAN equilibrium constant was taken from Tyndall et al. This constant is massively temperature dependent, mainly due to the temperature dependence of the dissociation of PAN, which varies by 9 (nine) orders of magnitude between 210 and 310 K. Why take Tyndall and not JPL-NASA ? How dependent are the results on the choice of Keq ?

Thanks to the reviewer for inadvertently catching some incorrectly updated documentation. The rate was updated to JPL-06 in our version of GEOS-Chem. The same rate is recommended in JPL-11. We have changed the text description to:

"To describe this chemistry, GEOS-Chem uses the recommendation from Sander et al., (2011), which is taken from Bridier et al. (1991). The parameters recommended by Bridier et al. (1991) are consistent with later studies of PAN decomposition by Roberts and Bertman (1992), Orlando et al. (1992), and Grosjean et al. (1994)."

Sander, S. P., J. Abbatt, J. R. Barker, J. B. Burkholder, R. R. Friedl, D. M. Golden, R. E. Huie, C. E. Kolb, M. J. Kurylo, G. K. Moortgat, V. L. Orkin and P. H. Wine "Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation No. 17," JPL Publication 10-6, Jet Propulsion Laboratory, Pasedena, 2011 http://jpldataeval.jpl.nasa.gov.

P26850, L5. Short lived HCs are added to the suite of species emitted from fires. What were these trace gases ? Is there an observational basis for this or were they simply added to increment the PAN production rate ?

Yes, this is confusing as written. We have changed the wording. These trace gases are only what is listed in Table 1, there were no additional species added. As indicated earlier in the text, primary NMVOCs in the standard GEOS-Chem mechanism that contribute to PAN formation include ethane, propane, $>C_3$ alkanes (lumped), $>C_2$ alkenes (lumped), isoprene, acetaldehyde, methylglyoxal, acetone, and $>C_3$ ketones (lumped). Our extended mechanism adds several additional primary NMVOCS including ethanol, benzene, toluene and ethylbenzene (lumped), xylenes and trimethyl benzenes (lumped), and monoterpenes (lumped). So in reference to biomass burning emissions, these additional species are also emitted from biomass burning. The lifetime of the aromatics and lumped terpene species are shorter than the other species emitted from fires in the standard GEOS-Chem mechanism.

Likewise, 35 % (by mass) of the biomass burning plumes from Boreal fires were distributed above the BL. Is there any basis for this fraction, or was it simply adjusted to get the best model-observation agreement for PAN ?

We actually tested several options here. In short, PAN is sensitive to this choice, but fire injection height can't be chosen based on the PAN data. There are too many other factors that impact PAN. We do know that emitting this critical portion of smoke above the boundary layer extends the lifetime of PAN. We settled on 35% based on Val Martin et al. (2010)'s designation of smoke clouds. Using 5 years of fire plume heights for North America derived from the Multi-angle Imaging Spectro Radiometer (MISR) instrument onboard the Terra satellite, Val Martin et al. (2010) showed that a substantial fraction of plumes from fires (4-12%) are injected into the free troposphere. Smoke plumes over the boreal region reached the highest altitudes. Analysis of smoke clouds, which are a later stage of plume evolution and what we are trying to capture at this coarse model resolution, indicated that ~35% were above the boundary layer. This is likely conservative because the Terra satellite overpass time is not in the afternoon when fires have typically reached their maximum intensity.

P26853, L17. Modelled PAN is shown to be very sensitive to HO2 uptake, though the latter appears to be poorly characterized. What do the kinetic evaluation panels say about this ? Is taking an extreme value (1) for the uptake coefficient a good way to examine model sensitivity ?

Thanks for this comment. Since this paper was submitted, there are three new publications to cite. We have added the following sentence to this text. It is unclear whether there is a better way to test model sensitivity than our two implementations.

"This new HO_2 *uptake scheme is recommended in the most recent IUPAC literature (Ammann et al, 2013), and also consistent with recent studies over East Asia (Guo et al, 2013; Liang et al., 2013)."*

References

Ammann, M., Cox, R. A., Crowley, J. N., Jenkin, M. E., Mellouki, A., Rossi, M. J., Troe, J., and Wallington, T. J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume VI – heterogeneous reactions with liquid substrates, Atmos. Chem. Phys., 13, 8045-8228, doi:10.5194/acp-13-8045-2013, 2013.

Guo, J., A. Tilgner, C. Yeung, Z. Wang, P. K. K. Louie, C. W. Y. Luk, Z. Xu, C. Yuan, Y. Gao, S. Poon, H. Herrmann, S. Lee, K. S. Lam, and T. Wang, Atmospheric Peroxides in a Polluted Subtropical Environment: Seasonal Variation, Sources and Sinks, and Importance of Heterogeneous Processes, Environmental Science & Technology, 10.1021/es403229x, 2013.

Liang, H., Z. M. Chen, D. Huang, Y. Zhao, and Z. Y. Li: , Impacts of aerosols on the chemistry of atmospheric trace gases: a case study of peroxides and HO_2 *radicals, Atmos. Chem. Phys., 13(22), 11259-11276, doi:10.5194/acp-13-11259-2013, 2013.*

P26857,L22. isoprene and monoterpenes are important precursors for PAN formation. This statement is followed by text which described schemes for isoprene degradation, but not for terpenes. From page 26847 the authors use RACM2 scheme for terpenes. What are the PAN precursors resulting from terpene degradation in this scheme and how well are they known?

We have added the following to the text:
"The gas phase oxidation of monoterpenes is highly unconstrained. The RACM2 mechanism is primarily based on Atkinson and Avery (2003). The yields of the immediate PAN precursors resulting from terpene degradation as described by RACM2 embedded in GEOS-Chem are given in Table 1. The mechanism produces methyl ethyl ketone and acetone, both of which can serve as PA radical precursors. The addition of this lumped terpene increases PAN in the model. The largest surface changes for PAN are for Eastern Europe and Western Russia, where there are high biogenic terpene emissions but there is little PAN data for comparison."

Atkinson, R. and J. Arey: Gas-phase tropospheric chemistry of biogenic volatile organic compounds: a review, Atmospheric Environment, 37 Supplement No. 2, S197-S219, 2003.