Interactive comment on “Atmospheric peroxyacetyl nitrate (PAN): a global budget and source attribution” by E. V. Fischer et al.

Anonymous Referee #2

Received and published: 6 December 2013

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 (P26662, 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.

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?

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?

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? 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?

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?

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?

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 26841, 2013.

C9750