

Effects of biogenic nitrate chemistry on the NO_x lifetime in remote continental regions (E. Browne et al.).

Browne et al. present an interesting analysis of the impact of organic nitrates on ozone in remote regions. They first use a steady state model to diagnose the role of organic nitrates. They then expand their analysis using a regional 3D model. The topic of this study is within the scope of ACP. However, I believe the 3D model section should be significantly expanded before publication.

1. p 20680 line 17
have the nighttime performance of WRF been evaluated? If so provide a reference.
2. p 20681 line 9
the major role of RONO₂ at low NO_x is partly driven by the decrease in OH. There is a lot of uncertainty regarding OH concentrations under low NO_x conditions, especially in the biogenic rich environments the authors focus on. Could the authors comment on the sensitivity of their results to OH concentrations under low NO_x ? How does the use of a faster isomerization rate for isoprene peroxy radicals affect their results (e.g., [3]). One would expect a much more limited influence of organic nitrate (greater OH concentrations, smaller fraction of RO₂ reacting with NO).
3. p 20682 line 22
I was expecting HNO₃ production to be very sensitivity to P(HO_x) under low NO_x conditions, yet the authors suggest it is not. Could the authors clarify the mechanism at play?
4. p 20684 eq. 5
 - (a) It seems to me the α in eq. 5 is different from α in R3a. This is because RONO₂ is considered a terminal NO_x sink in the chemical mechanism used in the steady state mechanism, while (as noted by the authors later), there are evidence many RONO₂ can be photooxidized quickly. Hence, I believe α (eq. 5) represents the overall loss of NO_x following RONO₂ formation. This should be clarified.
 - (b) Following on the previous comment, the steady state model does not represent the dependence of α (eq. 5) on OH (and other oxidants): under low OH, RONO₂ behaves like a terminal sink, while under higher OH, it can be seen as a temporary reservoir (thus reducing α). This effect may account for some of the differences between the steady state and WRF-Chem results.
5. Section 6
The authors use a 3D model to illustrate the applicability of the conclusions derived from the steady state model. I think this study would greatly benefit from a more thorough discussion of the results of the 3D model.

- (a) to my knowledge, WRF-Chem has not been evaluated in boreal regions. The authors should present a short comparison between models and observations (ozone, alkyl nitrate), to convince the reader the model performs reasonably well and then illustrate the sensitivity of boreal ozone to the treatment of alkyl nitrates (cf. point (c))
- (b) many chemical transport models do not include a specific treatment of terpenes and it would be of interest to show how sensitive boreal ozone is to their chemistry. How does the OPE change when terpene chemistry is included? Can this change be attributed to changes in the local removal of NO_x (through RONO₂), the local production of O₃ (through increase in P(RO₂)), and the long-range of transport of organic nitrate (including PAN)? How sensitive are those conclusions to uncertainties in chemical mechanisms, e.g., terpene chemistry, OH concentration under low NO_x?
- (c) a new detailed mechanism of isoprene/terpene chemistry is used. It is essential that this mechanism be properly documented. This is especially critical for terpene chemistry, where this study relies on unpublished work (RACM2, future work by the authors). Alternatively and keeping with the mechanistic focus of this study, I would suggest to use an already published simplified treatment of terpene chemistry (e.g., from [1]).

6. p 20688 line 9

I am not convinced by the importance of NO_x removal by organic nitrates to reconcile measured and simulated preindustrial ozone

- (a) the largest discrepancy is in the winter, when biogenic VOCs are low
- (b) Mickley et al. [2] did include isoprene and terpene nitrates. Could the authors elaborate on the differences between their mechanisms and that of Mickley et al.? I would actually expect the discrepancy between model and measurements to be larger with the authors' more realistic treatment of BVOC chemistry.

References

- [1] A. Ito, S. Sillman, and J. E. Penner. Effects of additional nonmethane volatile organic compounds, organic nitrates, and direct emissions of oxygenated organic species on global tropospheric chemistry. *J. Geophys. Res.*, 112:D06309, March 2007.
- [2] L. J. Mickley, D. J. Jacob, and D. Rind. Uncertainty in preindustrial abundance of tropospheric ozone – Implications for radiative forcing calculations. *J. Geophys. Res.*, 106(D4):3389–3399, 2001.
- [3] D. Taraborrelli, M. G. Lawrence, J. N. Crowley, T. J. Dillon, S. Gromov, C. B. M. Grosz, L. Vereecken, and J. Lelieveld. Hydroxyl radical buffered

by isoprene oxidation over tropical forests. *Nature Geosci*, 5(3):190–193, 03 2012.