Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on "Organic nitrate chemistry and its implications for nitrogen budgets in an isoprene- and monoterpene-rich atmosphere: constraints from aircraft (SEAC^{4}RS) and ground-based (SOAS) observations in the Southeast US" *by* J. A. Fisher et al.

Anonymous Referee #2

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Hydrolysis is receiving increased attention in chemical transport models as a way to remove organic nitrate (thus NOx) from the atmosphere by converting it to nitric acid. Hydrolysis that has been implemented in (CTMs) chemical transport models thus far (CAMx: Hildebrant Ruiz and Yarwood 2013, CMAQ: Pye et al. 2015) assumes that hydrolysis occurs after semivolatile organics partition to an organic-rich particle. The process of semivolatile organics (monoterpene-derived) undergoing hydrolysis has been demonstrated in laboratory work (e.g. Boyd et al. 2015, Bean and Hildebrandt Ruiz

2016). The timescales for hydrolysis used in CTMs ranges from 3 to 6 hours or longer. Thus, the work of Fisher et al., with a 1 hour hydrolysis represents a significantly faster rate of hydrolysis. Indeed, more than half of the organic nitrates in table 1 have a sub 2-hour lifetime. The irreversible reactive uptake formulation used by Fisher et al. also differs from the equilibrium vapor-pressure based approach. As a result, the Fisher et al. work represents a significantly different approach than has been used thus far for hydrolysis and creation of particulate organic nitrate. The implications for ozone and aerosol may motivate future work to adopt similar formulations and parameter choices should be fully justified.

My main question is whether or not another set of parameters than those examined here would provide equally good model performance. For example, there are no sensitivity simulations to indicate if the 1 hour hydrolysis is significantly better than say a 6 hour hydrolysis. It would be useful to know if another set of conditions (specifically lower BVOC emissions, higher NOx emissions, slower hydrolysis, slower uptake of organic nitrates) also leads to a consistent picture of southeast chemistry. More detailed comments follow.

Travis et al. is referenced as the basis for the gas-phase oxidant chemistry in this work. In that work, they indicate NOx emissions from the EPA NEI are too high by 50%. I assume the simulations in this work (Fisher et al.) reduce NOx emissions consistent with Travis et al. Given the suspected importance of reduced NOx emissions, I provide some comments on the Travis et al. paper (available at: http://acmg.seas.harvard.edu/publications/2016/Travis_ACPD_2016.pdf). Reducing the NEI NOx by ∼50% may imply a larger hydrolysis sink is needed in the model than is actually necessary. Comments on the Travis et al. paper:

1. Given the missing free tropospheric NO2 in GEOS-Chem and the fact that boundary layer NO2 is less than 30% of the column, how quantitative can the NO2 column evaluation be? What is the error associated with the BEHR and NASA columns? It seems like the GEOS-Chem shape factors may not be a good representation of the

NO2 profile given the lack of NO2 aloft. What is the detection limit/precision for surface NO2 from OMI?

2. The ratio of ISOPOOH to ISOPN seems degraded with the NOx emission reduction compared to the base indicating too much RO2+HO2 vs RO2+NO. Are there additional later generation products that can be examined to justify proper branching?

3. How does the magnitude of the soil NOx emission predicted in GEOS-Chem compare to other estimates? Does the NEI provide a comparable estimate?

Fisher et al. (this work) comments:

4. Figure S3 indicates too many pRONO2 compared to the AMS data during the day, particularly 13-17 local time. The diurnal profile of the model pRONO2 (relatively flat with peak around 15 local time) also doesn't match the observed AMS profile (peak at night around 3-4 am with minimum around 15 local time). Are the isoprene nitrates too aggressively put in the particle?

5. I recommend performing a total NOy and total inorganic nitrate (HNO3 + NO3-) evaluation. I didn't see a total NOy evaluation in either Travis et al. or Fisher et al. It was a little unclear if Travis et al. included all the updates (ie monoterpenes) of Fisher et al. In any case, Travis shows that HNO3 is high in the base. If the base includes hydrolysis, that may explain why. Furthermore, total RONO2 is underestimated by ~50% according to Figure 10. This implies there are missing NOx sinks (or sources) in the model.

6. Figure 12 shows that as the ratio of BVOC to NOx emissions increases, the fraction of NOx lost to RONO2 (vs HNO3) increases. If BVOC emissions are biased high (Fig 4 shows a NMB of 58% for isoprene and 18% for monoterpenes compared to DC8 flights) and NOx emissions are biased low (2011 NEI is reduced ~50%) then the model will predict too much NOx lost to RONO2 vs HNO3. Hydrolysis converts RONO2 to HNO3. Another set of BVOC and NOx emission levels and their evaluation would be useful.

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It would be nice to see analysis examining the possibility of lower BVOC emissions, higher NOx emissions, slower hydrolysis, and slower uptake of organic nitrates leading to a consistent picture of southeast chemistry.

7. Page 7, line 32: The yield of organic nitrates from API+NO3 is set to 10%. This seems to be on the low end considering the values tabulated in Fry et al. 2014 which range from 11-29% for a-pinene and 40-74% for b-pinene. Is there a specific RO2 fate assumed for these yields?

8. Page 8, line 33: Is there a figure that can be referenced to show good RONO2 performance?

9. Page 9, near line 7, how was the specific lifetime of 1 hour against hydrolysis chosen? Were other values used in preliminary simulations? For the isoprene system, what is the fraction of tertiary vs. non-tertiary nitrates?

10. Page 9, line 16, in reality, the hydrolysis lifetime should affect gas-phase RONO2. In the reactive uptake formulation of Marais et al. the uptake coefficient depends on the rate of particle-phase reaction (here hydrolysis). Faster reaction increases the uptake coefficient. It should be pointed out that this dependence of gamma on hydrolysis is not captured by the model.

11. Page 13: Are the TD-LIF measurements of total ANs consistent with the SEARCH network measurements during SOAS?

12. A few things indicate the NOx emissions may have been reduced too much:

o the total ANs are low by ~50% (Figure 10)

o The ratio of ISOPOOH to ISOPN seems degraded (too high) with the NOx emission reduction compared to the base (Travis et al. Figure 2)

o The NO2 columns are low compared to observations (Travis et al.) and the ability of the satellite products to determine the magnitude of a given error in surface NO2 is

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unclear

o A source of HNO3 (hydrolysis) must be added to the model

13. In addition to posting the mechanism online, can full details be provided in the supporting material for future reference?

14. While I am aware of studies of isoprene nitrates undergoing hydrolysis in bulk systems (e.g. Jacobs et al. 2014 ACP), what studies explore the interaction of gas-phase isoprene nitrates and aerosol-phase hydrolysis products for the isoprene system?

References

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Jacobs, M. I., Burke, W. J., and Elrod, M. J.: Kinetics of the reactions of isoprene-derived hydroxynitrates: gas phase epoxide formation and solution phase hydrolysis, Atmos. Chem. Phys., 14, 8933-8946, doi:10.5194/acp-14-8933-2014, 2014.