Response to Short Comment by Tim Canty

<u>Comment</u>: *This is a very interesting paper and an admirable endeavor to extend CMAQ to hemispheric scales. I was especially interested in the handling of alkyl nitrate lifetime. Our group has done similar analysis of alkyl nitrates with comparisons to satellite and aircraft observations in using the CMAQ with CB05 chemistry and CAMx with CB6r2 chemistry (Canty et al., 2015, Goldberg et al., 2016).*

What is the lifetime of NTR in this new model framework? Our modification of NTR so that its lifetime is much shorter (~1 day), expected if hydroxynitrates are the most abundant species, has led to a better representation of NTR in CB05 when compared to aircraft observations taken during DISCOVER-AQ. Across our model domain, tropospheric column NO2 from CMAQ was in better agreement with satellite observations when the NTR lifetime was decreased. The faster decomposition of NTR also led to an increase in modeled surface ozone. Based on this, the decrease in ozone reported in Fig 4 of this manuscript was a surprise. Is this decrease due to transport or to increased deposition processes? The improved speciation of NTR in the CB6r2 chemical mechanism led to a shorter lifetime of NTR, in the model, without any needed changes to the NTR chemistry. Great job with this analysis!

<u>Response</u>: Thank you for the positive comments on the manuscript and the analysis. We are aware of the analysis reported in Canty et al. (2015) and read with interest the work reported in Golberg et al. (2016). As discussed in our manuscript and previously (Schwede and Luecken, 2014; Canty et al., 2015, Appel et al., 2017), a thorough description of the NTR family of gases is needed to accurately represent their atmospheric lifetimes and rate of NOx recycling that eventually will influence O_3 distributions on local to hemispheric scales. As indicated in the discussion, both physical and chemical sinks of NTR influence its atmospheric lifetimes, but an important distinction is that chemical sinks recycle back NO_x (on varying time scales) while the physical sinks (wet and dry deposition) do not. Clearly, the relative roles of these two NTR removal processes depend on the form of the organic nitrate species. In our initial implementation, we followed Xie et al. (2013) and modified the rate constant for the NTR+OH reaction to that for isoprene nitrates, since on the hemispheric scales organic nitrates formed from isoprene are the largest contributor to the simulated tropospheric NTR burden. More importantly, the dry deposition velocity for NTR was mapped to that for HNO_3 and the Henry's law constant for NTR was also mapped to that of HNO_3, thereby enhancing wet scavenging of NTR. Thus, for the calculations based on these assumptions, at least at the surface one can expect the lifetime of NTR to be comparable to HNO_3 and on the same order or shorter than what was invoked by increasing its photolysis rate by a factor of 10 in your analysis. However, unlike your approach which recycles the NOx back more rapidly locally, an important distinction is that the enhancement of the physical sinks removes the reactive nitrogen from the atmosphere. Thus on the hemispheric scales, less NOx is recycled (due to lower amounts of NTR) and so there is lower ozone shown in Figure 4.

Recently, in CMAQ we have replaced the single alkyl nitrate species (NTR) in CB05TU with seven species to better capture the range of chemical reactivity and Henry's law constants (and thus the physical sinks) – see Appel et al. (2017, GMD). We believe such an approach helps better regulate the organic nitrate budget (also evaluated through comparisons with wet deposition measurements), increases the amount of NO_x recycled locally (resulting in local increases in O_3), but reduces the NTR burden on the larger hemispheric scale and better modulates hemispheric background O_3. The impacts of the rate of NOx recycling from organic nitrates is also seen in the RACM2 results presented in Figure 12, which show higher O_3 in polluted regions, but lower values are seen in the remote areas relative to the CB05TU mechanism; these differences in part arise from higher rates of NO_x recycling from organic nitrates in RACM2 relative to CB05TU. The recently released version of CMAQ (v5.2) includes the CB6 mechanism with updated organic nitrate chemistry; application and evaluation of the CB6 mechanism over hemispheric scales is currently underway.