

Interactive comment on “Examining the impact of heterogeneous nitryl chloride production on air quality across the United States” by G. Sarwar et al.

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Anonymous Referee #2

Comment: This paper describes the incorporation of a ClNO₂ production mechanism and additional Cl atom + VOC reactions into an air quality model (CMAQ) and explores the impact of specifically the heterogeneous production of ClNO₂ on ozone and particulate nitrate. This represents the most advanced treatment of this chemistry in a large-scale air quality and thus is an important contribution. The paper is clearly written and the conclusions are generally in concert with the results and experiments conducted with the model. Given that this one process leads to significant changes in

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modeled ozone and nitrate, and that the approach to incorporate it into models is well described, the results are important and useful for the community. I thus recommend publication after the authors address some comments and concerns described below.

Response: We appreciate the reviewer's thoughtful comments and suggestions to improve the article.

Major Comments

Comment: The authors focus almost entirely on describing changes to mean ozone or mean daily maximum O₃ or particle nitrate. They do describe a few "event" days. Both ozone and nitrate, and especially ozone, are rather insensitive to many individual chemical processes. Even if North American anthropogenic emissions are zero, mean O₃ might change only by 50% at most at many locations across the U.S. See e.g. Zhang et al Atmos. Env. 2011. Wouldn't the interest therefore be the extent to which this process impacts "non-background" ozone or nitrate? Would the sensitivity to local NO_x emissions be different in this context than what is implied by comparing to mean O₃? Does the probability of O₃ violation become sensitive to on shore wind speed (i.e. sea salt flux)? Basically, I feel some sort of justification for the utility of the chosen focus is in order.

Response: We believe that we have struck a good balance of showing both the range of ozone responses (by showing time series for the entire modeled period of ozone/nitrate changes for particular areas in Figure 6 and by showing average diurnal profiles of ozone changes in areas that have large responses in Figure 7) and "typical" ozone changes by showing the mean response. We feel that by showing both types of information the reader is presented with a full picture of how ozone responds to this chemistry. Since our "average" change in ozone and nitrate in Figures 4 and 8 are given in absolute units (ppb and microgram/m³), this value is the same whether we compare it to total ozone or "non-background" ozone. We agree that the absolute changes in ozone due to this chemistry would make up a relatively larger portion

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of "non-background" ozone than of "background" ozone. However, quantifying background ozone levels is an analysis that would require additional modeling runs, involves some controversy in the most appropriate way to define "background" and is beyond the scope of this work. Furthermore, ClNO₂ chemistry has the potential to affect both background and non-background ozone so we believe that making the distinction of ozone changes only with respect to "non-background" ozone concentrations is not appropriate for this analysis.

Minor Comments

Comment: 6157 line 7 – Have NMB (and NME later) been defined?

Response: NMB and NME are currently described in Table 2. We now define it in section 3.2 as follows: The heterogeneous production of ClNO₂ marginally affects model performance statistics for daily maximum 8-h O₃. For example, it changed the Normalized Mean Bias (NMB) (Eder and Yu, 2006) (from –20.2% to –18.8% in February and 0.1% to 0.4% in September for observed values above 65 ppbv. These changes which are mapped in Fig. S1 show that improvements and degradations in model performances do not have a noticeable geographic pattern. The inclusion of heterogeneous ClNO₂ formation also changed Normalized Mean Error (NME) (Eder and Yu, 2006) both in February and September by similar margins.

Comment: 6158 line 19 – 20. This conclusion seems rather tenuous. The authors are using the response of ozone and nitrate – likely not terribly sensitive to ClNO₂ formation to assess what limits ClNO₂ formation. Wouldn't the better experiment be to vary particle chloride, and then separately vary NO_x?

Response: We removed line 19-20 and replaced it with the following sentence: These results suggest that the heterogeneous production of ClNO₂ can further increase O₃ and reduce TNO₃ if elevated particulate-chloride levels are present in the atmosphere.

Comment: 6159 line 1 – 2. This is essentially the claim in Thornton et al Nature 2010

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– is there a quantitative consistency between this work and that?

Response: We add following sentences for comparison of our results to the findings of Thornton et al. (2010) in section 3.3: Thornton et al. (2010) calculated annual average ClNO₂ yield over the contiguous US by using a coarse grid-resolution (10x10) and constraining their predictions with observations from the Interagency Monitoring of Protected Visual Environments and the National Atmospheric Deposition Program. We calculate monthly averaged values for fine as well as coarse particles over the contiguous US by using a finer grid-resolution (12-km x 12-km). Thus, these values cannot be directly compared, so a qualitative comparison of these yields is made. Our predicted values are consistent with the calculation of Thornton et al. (2010) over the coastal areas; both studies suggest relatively higher values over the coastal areas in the US. While our study suggests values can be high in the entire eastern US in February (fine particles), Thornton et al. (2010) calculates higher values only in the southeastern US. Thornton et al. (2010) suggests higher values throughout the western US while our study suggests higher values over much of the West, but very low yields in the desert southwest.

Comment: 6159 lines 9 – 12. Is "mean" really a useful metric here since for 12 hours the concentration is 0? I would recommend mean daily maximum as a metric that is more comparable to field observations and its potential importance. Indeed the authors use this later to compare to observations.

Response: As suggested, we revised the Figure and relevant discussion using mean of daily maximum ClNO₂ as follows:

Modeled mean of daily maximum ClNO₂ levels in the base simulation that included only the gas-phase formation pathway (no heterogeneous ClNO₂ production) were negligible (generally <5 pptv) and are not discussed further. Heterogeneous production enhanced ClNO₂ levels both in February and September. Predicted monthly mean and max of daily maximum ClNO₂ levels with the heterogeneous production are pre-

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sented in Fig. 1. ClNO₂ formed where particulate chloride and NO_x concentrations are prevalent. The highest monthly mean ClNO₂ was found in the Los Angeles area both in February (~1.0 ppbv) and in September (~1.5 ppbv). Mean ClNO₂ concentrations also reached values of 0.24 to 0.48 ppbv in portions of the Northeast during both September and February. While predicted values reached higher concentrations in September, predicted levels are more spatially distributed in February. The maximum hourly predicted value in February reached almost 3.0 ppbv in Los Angeles and 2.0 ppbv in the Midwest. High hourly ClNO₂ concentrations in September were found in Idaho (4.5 ppbv maximum) and in Los Angeles (4.0 ppbv maximum). Predicted ClNO₂ levels were consistently high in Los Angeles both in February and September. Available chlorine to produce ClNO₂ in coastal areas comes from sea-salt emissions and in the Midwest comes from anthropogenic chloride emissions. In addition, chlorine available to enhance ClNO₂ over the eastern half of the United States in February is due to anthropogenic emissions and over Idaho is due to chlorine emissions from the forest fires in September.

Comment: 6163 – 6164: Again Thornton et al make a prediction in this regard, something like up to 20% of NO_x may be as ClNO₂ (not in a 24-hr mean sense). How do those predictions compare? Also the use of mean here again seems rather useless because NO_y is dominated by compounds with relatively much smaller temporal variability (NO₂, PAN, Nitrates, HNO₃) while ClNO₂ reaches a maximum and decays to zero on the timescale of 12 hrs. Mean maximum ratio is probably more useful.

Response: As suggested, we calculated monthly mean of daily maximum ClNO₂:NO_y ratios and revised the section as follows:

The monthly mean of daily maximum ClNO₂:NO_y ratios without the heterogeneous ClNO₂ production were negligible (< 0.005). Heterogeneous ClNO₂ production increased monthly mean of daily maximum ClNO₂:NO_y ratios up to 0.06 in February as well as in September. Higher ClNO₂:NO_y ratios occurred over a larger geographic area in February than those in September. As TNO₃ concentrations decreased with the

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heterogeneous ClNO₂ production, so did their contribution to NO_y. While the monthly mean daily maximum ClNO₂:NO_y ratio reached only up to 0.06, the maximum hourly ClNO₂:NO_y ratios are much greater and reached 0.34 in February and 0.17 in September. The contribution of ClNO₂ to NO_y was greater in February than in September; thus, the ratio was also generally higher in February. Our predicted maximum hourly ClNO₂:NO_y ratios agree well with the results of Thornton et al. (2010) who suggested up to 22% of NO_x may be cycled through ClNO₂.

Comment: 6164 – I think it would be useful to give the full decrease in nitrate not just the additional decrease compared to the simulations above. What exactly is different about the two parameterizations – can this be summarized? Is one more realistic, i.e. just because it further decreases model biases of nitrate is it for the right reasons? The impression here is that Bertram and Thornton is an improvement because it can reduce nitrate biases without increasing O₃ significantly. But it would be good to know if that parameterization is ignoring some other processes which the Davis parameterization includes or vice versa.

Response: We provide the full decrease in nitrate in Figures 2 and 3 (these figures will be added to the supplemental file) and revise the section as follows:

The presence of particulate chloride can increase γ N₂O₅ as described by Bertram and Thornton (2009). However particulate chloride is not explicitly accounted for in the γ N₂O₅ which is described by Davis et al. (2008) and used in the current version of CMAQ. The Davis et al. (2008) parameterization accounts for sulfate, nitrate, ammonium, and water, phase of the PM (ice versus aqueous) and temperature. However, it does not account for the effect of particulate chloride on γ N₂O₅. Bertram and Thornton (2009) account for the effect of particulate chloride on γ N₂O₅ but neglect the effects of temperature, PM phase, sulfate, and ammonium. Both parameterizations account for decreasing γ N₂O₅ with increased nitrate concentrations, but the Bertram and Thornton (2009) formulation is based on a mechanistic description of the nitrate inhibition effect while Davis et al (2008) uses a linear relationship. The Davis et al.

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(2008) parameterization was also used to calculate the heterogeneous reaction rate on fine particles in this work. To evaluate the sensitivity of the model results to $\gamma\text{N}_2\text{O}_5$, two additional simulations were completed for a 10-day period in each month. The first simulation employed $\gamma\text{N}_2\text{O}_5$ (Eq-4) of Bertram and Thornton (2009) on both fine and coarse particles and used $Y = 0$. The second simulation employed $\gamma\text{N}_2\text{O}_5$ of Bertram and Thornton (2009) on both fine and coarse particles with Y calculated using Eq 3. The differences in results obtained with the two simulations are compared to those obtained with the previous two simulations employing $\gamma\text{N}_2\text{O}_5$ of Davis et al. (2008) on fine particles and $\gamma\text{N}_2\text{O}_5$ of Bertram and Thornton (2009) on coarse particles. While enhancements in hourly O_3 obtained with the two $\gamma\text{N}_2\text{O}_5$ varied occasionally by 1-2 ppbv, the enhancements in mean 8-hr O_3 obtained with the two $\gamma\text{N}_2\text{O}_5$ formulations did not differ significantly (<0.2 ppb). The decreases in mean TNO_3 obtained with the $\gamma\text{N}_2\text{O}_5$ of Bertram and Thornton (2009) on both fine and coarse particles were greater than those obtained with the modeling simulations described in the main portion of this paper (Figures 2 and 3). Thus, the use of $\gamma\text{N}_2\text{O}_5$ of Bertram and Thornton (2009) on both fine and coarse particles can further reduce TNO_3 without further enhancement of O_3 .

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 6145, 2012.

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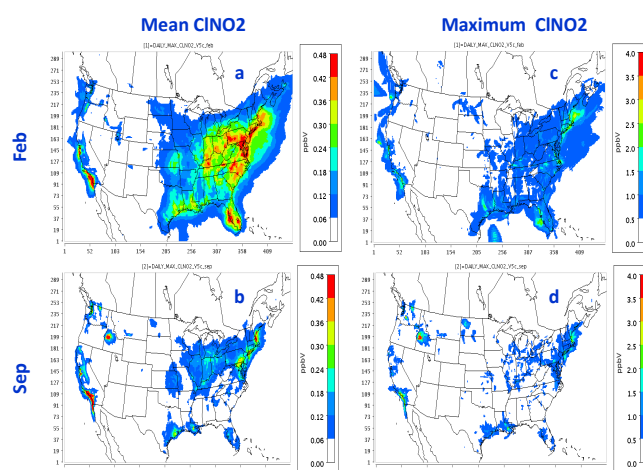


Fig. 1. Predicted mean of daily maximum CINO2 in (a) February (b) September. Predicted hourly maximum CINO2 in (c) February (d) September.

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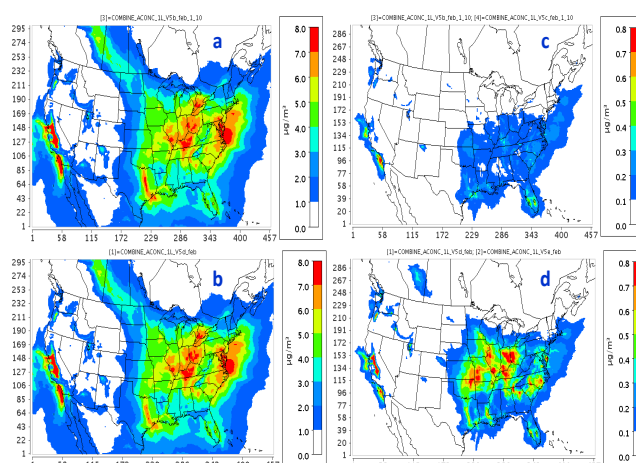


Fig. 2. February: (a) and (c) mean TNO3 and changes in TNO3 due to het. CINO2 with gamma of Davis et al. and Ber. & Tho. (b) and (d) mean TNO3 and changes in TNO3 due to het CINO2 with gamma of Ber. & Tho.

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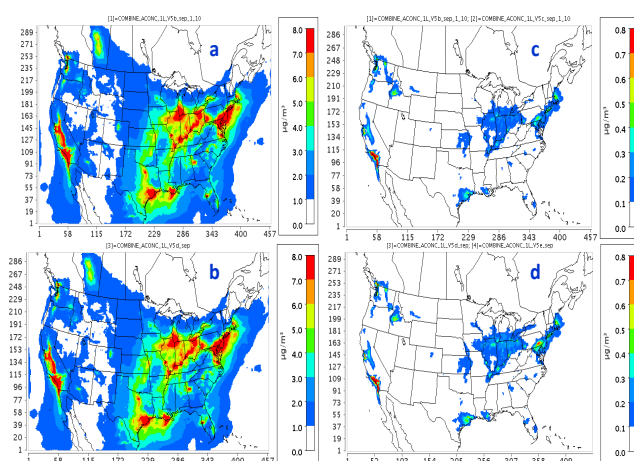


Fig. 3. September: (a) and (c) mean TNO3 and changes in TNO3 due to het. CINO2 with gamma of Davis et al. and Ber. & Tho. (b) and (d) mean TNO3 and changes in TNO3 due to het CINO2 with gamma of Ber. & Tho.

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