

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

Anonymous Referee #2

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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 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.

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Major Comments 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 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.

Minor Comments 6157 line 7 – Have NMB (and NME later) been defined?

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?

6159 line 1 – 2. This is essentially the claim in Thornton et al Nature 2010 – is there a quantitative consistency between this work and that?

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.

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

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of 12 hrs. Mean maximum ratio is probably more useful.

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.

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