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Atmospheric Chemistry and Physics Discussions

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 #3

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General comments

This paper presents a continental scale model of the influence of ClNO2 formation and photolysis on ozone and particulate nitrate. The paper presents model results from two months, February and September 2006. The choice of these two months facilitates comparison with the limited field data for ClNO2 currently available (Houston, TX in September 2006, Boulder CO in February 2009, Calgary, Canada in early spring 2010). Predicted and observed ClNO2 levels agree well enough to justify the use of this model for further predictions of impacts of its formation. The model finds a modest influence of ClNO2 production on ozone averaged across the domain, with larger effects for

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specific days and within specific grid cells (e.g., Los Angeles). It also finds a modest influence on particulate nitrate, especially in winter. Since the only previous air-quality model analysis of the influence of ClNO2 was for specific conditions in Houston, TX, this paper is a new and useful contribution that will help to define the impact of this chemistry on air quality models.

The methodology and improvements to the chemical mechanism to include chlorine chemistry is well described. The only potential inconsistency is the treatment of the partitioning between gas phase HCl and particulate chloride, which is not described in detail (see comments below). The only potential omission is some discussion of the vertical distribution and mixing of pollutants (NOx and chloride) that produce ClNO2 in a poorly mixed nighttime boundary layer structure. This aspect was identified as a potential uncertainty in the prior work of Simon et al. and should be mentioned here as well to the extent that it was considered in this study.

Specific comments

Page 6152, line 5: ClNO2 influences ozone by producing radicals (source) and by reacting with O3 (sink). In the later model analysis, is there a way to separate the magnitude of the two effects? In other words, is the modest effect determined here due to approximately equal ozone sources and sinks, or to a small source countered by a much smaller sink?

Page 6153, reaction (R9). This reaction is typically written as between NO2+ and liquid water rather than NO2+ and OH-.

Page 6155, top. Chlorine mass is conserved between ClNO2 and particulate chloride. Does the model include a gas phase reservoir of HCl, as implied by the field observations? Is there explicit repartitioning between HCl and particulate chloride? Does this affect mass balance?

Section 3.1: Same comment. Is there any prediction of the gas-phase HCl reservoir

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associated with the modeled particulate chloride? Gas phase HCl is likely a better predictor of ClNO2 formation potential from a mass balance standpoint than is fine mode particulate chloride.

Page 6158, end of section 3.2: Is it possible to be more quantitative about the last statement? For example, is the integrated N2O5 production available from the NOx inventory and the amount of this NOx oxidized through N2O5, and can this number be compared with the chlorine / chloride inventory? Such a comparison may identify regions that are more or less Cl limited relative to NOx. It may also require substantial effort that is beyond the scope of this manuscript, so this comment is at the author's discretion.

Section 3.3, Figures 2, 3: Legends on the color scales are difficult to read and should be printed with larger font size. Modeled yields of ClNO2 are large in many regions – does the ClNO2 formation deplete particulate chloride over the course of individual nights?

Figure 3 also shows no ClNO2 in Colorado, though the text cites levels roughly in agreement with field observations there. Why the difference?

Section 3.4: Is it possible to determine the individual contributions of the Cl atom input and the recycling of the NO2 to increased ozone production? Another way to ask this question: Is the next day ozone model more sensitive to inclusion of ClNO2 (Cl atom source plus NOx recycling) or to changes in the uptake coefficient for N2O5 (NOx recycling only)? Again, although this would be a useful metric from a chemical mechanism standpoint, it is at the author's discretion to determine if it fits within the scope of the paper.

Page 6163, section 3.4.4: There are larger effects on ozone within certain grid cells. Is ClNO2 likely to influence the number of days above the air quality standards in Los Angeles?

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