Atmos. Chem. Phys. Discuss., 12, C3284–C3287, 2012
www.atmos-chem-phys-discuss.net/12/C3284/2012/

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.

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Received and published: 5 June 2012

Anonymous Referee #1

Comment: In response to the recent observation of prominent levels of nitryl chloride (ClNO2), the goal of the work by Sarwar et al. is to develop a chemical mechanism suitable for regional air quality models that takes into account the production of ClNO2 through the heterogeneous hydrolysis of N2O5. The new mechanism expands upon the existing CB05TU mechanism for gas-phase reactions and now includes chlorine-related reactions. As for the heterogeneous reactions, the existing CMAQ configuration is augmented with added yields for ClNO2 production, which in turn reduce HNO3

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production. The newly developed chemical mechanism is tested through the implementation in the Community Multiscale Air Quality (CMAQ) modeling system (version 5.0 beta) for a modeling domain that spans the whole United States. Two simulation periods are considered: February and September 2006. The model performance of the new parameterizations and relevant chemical mechanism updates is evaluated based on ClNO2 predictions as well as predictions for secondary pollutants, ozone and particulate nitrates.

Overall, the manuscript provides a comprehensive overview of the methodology for the development of the new mechanisms to account for ClNO2 production through heterogeneous N2O5 hydrolysis. Sufficient background of the scenario development, from emission inventory to meteorological conditions, is presented in the manuscript. The conclusions drawn from the analysis of the simulation results indeed demonstrate the importance to include the new mechanism for the improvement of air quality model performance. However, there are several questions that the authors should address, which would require some revisions to the manuscript:

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

Comment: In section 2.3, what is the motivation behind the decision to use the Davis et al. (2008) parameterization for fine particles and the Bertram and Thornton (2009) for coarse particles?

Response: The Davis et al. (2008) parameterization accounts for particle composition, phase of the PM (ice versus aqueous) and temperature. However, it does not account for the effect of particulate chloride on the heterogeneous uptake coefficient. Bertram and Thornton (2009) account for the effect of particulate chloride on the heterogeneous uptake coefficient but do not account for temperature or phase effects. Since the majority of the particulate chloride resides in coarse-mode sea-salt, we used the Bertram and Thornton (2009) parameterization for coarse particles. We felt that the effects of

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temperature and phase would be more important on fine particles than the chloride effect. In addition, the current CMAQ model uses the Davis et al. (2008) parameterization for fine particles. The model has undergone formal peer-review in its current form and is used by many users around the world. Thus, we decided not to change the heterogeneous uptake coefficient for fine particles.

Comment: In section 3.2, the statement "all current γN2O5 parameterizations, available in the peer-reviewed literature, produce higher γN2O5 values" is made without any reference. What about γN2O5 values for organic particles? They have been shown to have significantly lower γN2O5 compared to inorganic particles, see for example Chang et al., Aerosol Science and Technology, 45:655–685, 2011.

Response: We revise the sentence as follows: All current γN2O5 parameterizations, available in the peer-reviewed literature, produce higher γN2O5 values (Brown et al., 2006; Chang et al., 2011). Coatings of particles by organic materials have been suggested to lower γN2O5 values (Anita et al., 2006; Chang et al., 2011). However, the effect of organic particles on γN2O5 is not included in the current CMAQ model.

Comment: The discussion in section 3.6 mentioned that the enhancement of O3 obtained with the different γN2O5 value varied occasionally by 1-2 ppbv, and it is concluded that this is not much of an impact on O3. However, this seems to be on the same order of magnitude as the change in O3 between the base case and the heterogeneous ClNO2 production case (section 3.4.2). Please clarify why the differences due to γN2O5 are deemed to be negligible.

Response: Time series of the O3 increase due to the heterogeneous ClNO2 production in Los Angeles, Indiana, and Idaho (section 3.4.2 and Fig. 6) were obtained by averaging over each representative region (generally $\sim$100 grid-cells). Despite averaging over large spatial areas for Figure 6, the heterogeneous ClNO2 production enhanced O3 by up to 3.0 ppbv. When we used different γN2O5 in the model, hourly O3 in individual grid-cells occasionally increased by 1-2 ppbv. No spatial averaging

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was done to evaluate the impact of different γN2O5. If similar spatial averaging is done for O3 enhancement due to different γN2O5, impact is much lower. Thus, we considered the differences due to different γN2O5 to be less important than the impact of the heterogeneous ClNO2 production.

Comment: In Table 4, while the observed and modeled levels of ClNO2 are in reasonable agreement, model results seem to be consistently over-predicting ambient levels. Could this be quantified by the over-estimation of γN2O5? A discussion of this should be added to the manuscript.

Response: We add the following sentences in section 3.3: It should be noted that measured and predicted values can generally not be directly compared. For example, predicted values are hourly averaged while measurements are conducted at a much finer temporal resolution. Moreover, simulation and observed time periods are different (except for Houston, TX). Nevertheless, the model tends to generally over-predict ClNO2 compared to the observed data. Such over-predictions can be caused by several reasons including over-estimation of γN2O5 as indicated earlier.

Minor points:

Comment: Citation Davis et al. (2008), not (2010).

Response: We agree with the comment and plan to change it to Davis et al. (2008).

Comment: Page 6153, l.4: variable d has a tilde in the equation, but not in the explanatory text.

Response: We agree with the comment and plan to add tilde in the explanatory text.

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