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Atmospheric Chemistry and Physics Discussions

Interactive comment on "An MCM modeling study of nitryl chloride ($ClNO_2$) impacts on oxidation, ozone production and nitrogen oxide partitioning in polluted continental outflow" *by* T. P. Riedel et al.

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Response to Anonymous Referee #2

We thank Referee #2 for their careful reading of the manuscript and comments; below we provide responses to each comment individually.

General Comment by Referee #2:

Riedel et al. report the addition of chlorine chemistry to the Master Chemical Mech-

anism and apply the new mechanism to data collected during the Calnex-LA 2010 field campaign (focusing on the L.A. urban outflow). The new mechanism allowed the identification and prediction of concentrations of several halogenated VOCs produced during the Cl initiated oxidation of alkenes and of the nature and abundances of organic peroxy radicals produced. The authors confirm that the nocturnal conversion of N2O5 to ClNO2 and subsequent ClNO2 photolysis increases O3 production on the following day in the study region. The authors also show that about 3/4 of the Cl produced by morning ClNO2 photolysis converts to HCl, and that the remainder converts to ClO (via reaction of Cl with O3) or forms organochlorine molecules (via reaction of Cl with unsaturated hydrocarbons). Overall, the paper is written well, is thorough, and presents important results that should be published after my minor concerns below have been addressed.

Author responses follow each comment and are denoted with **.

General comments

1. The methodology used needs to be described in more detail. The additions are partly described on pg 28982 and in the supplement, but the paper is lacking a comprehensive table listing all of the reactions and rate coefficients that have been added to the model. Perhaps better still: Have the authors considered including the new MCM code as an appendix to this paper, or making it available for download on a web site or ftp server? After all, a considerable portion of this work is based on what was made freely available for download at the Leeds web site, and it would be a great service to the community if the authors were to follow the spirit of the MCM creators in this regard.

**We have added a table outlining all of the additional chlorine reactions and used rate constants not present in the native MCM to the supplemental information. The Matlab code containing the additional reactions and rate constants is also now freely available for download at: ftp://ftp.atmos.washington.edu/thornton/UWCM/UWCM_Riedel_etal_rxns.txt. We

have added the following statement to the manuscript communicating this. “A complete list of the added reactions and reaction rate constants is given in Supplemental Table S-2, and the MATLAB code is freely available for download at ftp://ftp.atmos.washington.edu/thornton/UWCM/.”

2. Calculated quantities were not compared with actual measurements. As such, the authors combined data from different measurement locations that are quite distant from each other. I agree that this was necessary to compensate for lack of certain measurements on the Atlantis. However, many of the estimated species used as model inputs and some of the species calculated (e.g., OH, HO2) were measured at the ground site. It would have made for a stronger and perhaps more interesting paper if the model presented here had been applied to and compared with measurements at the ground site only rather than to a mixed ship/ground site data set. Perhaps something that could be considered for a future paper.

**It is true that the majority of modeling papers focus on comparing model outputs to field measurements with an emphasis on reproducing the observations. However, in this study we did not intend for the model to reproduce the CalNex observations explicitly but instead aimed to base the model on a polluted coastal region similar to what was observed in the Los Angeles region during CalNex in order to investigate the general effects of halogen chemistry in such a region. “The goal of these modeling studies is not to replicate the evolution of specific air masses in the LA Basin, but instead to more generally probe the effect of multiphase reactive nitrogen and reactive halogen chemistry on radical budgets, ozone production, and the fate of NOx in polluted coastal regions.” We expect that future studies will explicitly compare to the observations at the ground site, but this type of box model is ill suited to that task given the need to faithfully represent hourly changes in transport and boundary layer dynamics.

3. In the model, the inclusion of Cl production (from ClNO2 photolysis) has an effect that lasts throughout the entire simulated day. Is this because there is more total Cl available in the model when ClNO2 is included?

**The referee is correct. The formation of ClNO2 indeed provides an additional source of reactive chlorine by activating particulate chloride to Cl-atoms following ClNOÂň2 photolysis. A portion of this additional reactive Cl then proceeds through the more labile reservoirs HOCl and ClONO2 which allow it to have a more lasting impact over the course of the model day. We address this with the statement: “To some extent these enhancements should be expected considering the larger Cl· pool available for recycling reactions when ClNO2 formation is allowed, but they give indication of the degree of indirect coupling between ClNO2 and Cl2 via the increased formation of reactive chlorine reservoirs like ClONO2 and HOCl.”

Specific comments

pg 28976 lines 8-9. "... the fate of the Cl radicals and the overall impact of ClNO2 on regional photochemistry remain unclear" Unclear may be a bit too strong a word considering that we do have knowledge of some, if not most, of the chemistry, and we do have a good notion of what impact ClNO2 has on regional photochemistry in general. Consider rephrasing this sentence, for example by replacing the word "unclear" with "poorly constrained by measurements and models."

**We have replaced “unclear” with “poorly constrained by measurements and models”.

pg 28976, line 24 - pg 2897, line 10. Oum et al. [Science, 1998] reported the existence of a photochemical source of molecular chlorine from photolysis of ozone on sea salt aerosol. Please state whether the latter has been included in this paper, and if not, why not.

**The model does not include a source of Cl2 from the photolysis of ozone in the presence of sea-salt particles as suggested by Oum et al. (1998). The Oum et al. (1998) study suggests a number of plausible mechanisms for Cl-atom production from O3 photolysis and subsequent heterogeneous reactions of H2O2 and/or OH with particle chloride to produce Cl2. Given the lack of a discrete mechanism to incorporate into the model we did not feel this potential source of Cl-atoms was complete enough to

reliably include in the model.

pg 28979, lines 10/11 Please balance the chemical reactions (e.g., R9 and R10 are missing O2 as reactant).

**We have added O2 over the reaction arrow.

pg 28980, lines 18-20. Some of the data sets mentioned have been described in the literature - e.g., Riedel et al., 2012a, Young et al., 2012, and Mielke et al., JGR, 2013. It would be appropriate to cite those papers here.

**We have added the suggested references.

pg 28981, lines 24-25. "Over the entirety of a model run temperature is held constant at 25 _C" The choice of temperature is critical as it affects reaction rates and model outcomes. A temperature of 25 _C seems too high for the nocturnal periods in this study region. Please include a sensitivity run at a lower temperature (e.g., +10 _C).

**As suggested we performed a model run for a 10 °C case. The lower temperature enhances N2O5 formation given the temperature dependent equilibrium between N2O5, NO3 and NO2. As a result, the maximum in ClNO2 and Cl-atoms increases by ∼30%. We have added the following statement to the main text to make this clear. “At lower model temperatures a larger fraction of NOx will react as N2O5 with higher ClNO2 levels and an increased morning Cl· burden relative to warmer cases. This result suggests that we are possibly overestimating the actual yield of ClNO2 per NO2 oxidized by ozone at night.”

pg 28982, lines 26 and 27. The IUPAC database is continuously being updated. Please state the version or year of the kinetics data used in this work.

**We have added the following clarifying statement. “The reaction rate constants and product branching for these reactions were taken from the IUPAC kinetics database as of May 11, 2012.”

pg 28983, line 1 "ClNO2 photolysis frequencies were estimated by scaling measured NO2 photolysis frequencies ... This approximation produces ... frequencies close to observations taken aboard the R/V Atlantis" Please explain why the ClNO2 photolysis frequencies were estimated even though they were measured. Also, the ClNO2 absorption cross-sections were recently revised by IUPAC (in June 2013). Were the most recent values used in this work?

**We chose to use the estimation as it allows the model to be more flexible for other investigations. Hardcoding the j-values measured by the R/V Atlantis into the model would have reduced the functionality of the model to accurately represent latitudes and solar declination angles significantly different from those of Los Angeles during May and June of 2010. These model results do not incorporate the June 2013 IUPAC revisions to the ClNO2 absorption cross-sections. These revisions are not expected to significantly affect the results presented in our manuscript as the revisions agree well with the previously used estimates.

pg 28983, line 5. ClONO2 and HOCl photolysis are mentioned here, but photolysis of Cl2 is not. Please describe how its photolysis frequency was determined.

**Cl2 photolysis frequencies were also determined using the TUV model. We have edited the manuscript to reflect this.

pg 28984, line 5. "Gas-particle reaction probabilities in the model are set to 0.01 for N2O5 ... ... is within the typical range ... (< 0.001 - 0.03)" This range is quite large. Please consider sensitivity runs at the extremes of this range.

**We agree the listed range in N2O5-aerosol reaction probabilities is large. That said, the given range represents N2O5 heterogeneous reaction probabilities over a large variety of different conditions (particle sizes, particle compositions, relative humidities, temperatures, and locations). Given the high levels of ClNO2 (>1 ppbv) in these polluted coastal regions, the N2O5-aerosol reaction probability in such regions must therefore be high enough to allow for such ClNO2 production. Please see our responses to

Referee #1 in this regard.

pg 28985 line 25. Please consider including a plot of the concentrations of ClNO2, ClONO2, HOCl, Cl2, OH, and CHOCl against hour of day from which the data in Fig 2 were derived.

**The suggested plot has been added to the supplemental information and referenced in the main text.

pg 28987 line 16 "the reaction of OH with formyl chloride ... becomes a noticeable Cl source" The authors speculate that this source may be higher in regions with alkene concentrations greater than Los Angeles. I am not sure I would agree considering that alkenes would also react with NO3, slowing down ClNO2 production.

**We agree that enhanced concentrations of alkenes could potentially result in an enhancement in NO3 reactivity that might decrease ClNO2 production. The effect will ultimately depend upon the abundance of NO2 relative to the alkenes. At high NO2, the impact of higher alkenes on NO3 lifetime will be somewhat buffered compared to the impact on Cl-atom reactivity.

pg 28988, paragraph starting on line 21 & Figure 4. It is difficult to follow this paragraph without knowing the concentrations of ozone, NO, NO2, HO2, and the various VOCs that were present in the model at 7 am and 3 pm. Consider calling out Figure S-9 earlier in the text and adding a table or graph with key molecules (e.g., ozone, NO, NO2, HO2) to accompany Figures 4 and S-9.

**As Figure S-9 is referenced in the same paragraph a few lines later we feel it is sufficient to direct the reader to the relevant Cl-atom reactivity information. As requested, we have added a plot of NO, NO2, and HO2 vs. model time to the supplemental information, and ozone mixing ratios are available in the newly added Supplemental Figure S-12 (see next comment).

pg 28992, "3.3 Impact on ozone production rate" The model predicts _10 ppbv of addi-

tional O3 as a result of ClNO2 chemistry (Figure 5C). To put this number in perspective, it would be useful to know how much total O3 the model produces in the absence of ClNO2 and in its presence, rather than only presenting the difference. Please consider adding this information to Figure 5, e.g., by modifying Figure 5C.

**We have added a plot of total O3 mixing ratios predicted by the model for the with- and without-ClNO2 cases to the supplemental information.

Sources cited:

Oum, K. W., Lakin, M. J., DeHaan, D. O., Brauers, T., and Finlayson-Pitts, B. J.: Formation of Molecular Chlorine from the Photolysis of Ozone and Aqueous Sea-Salt Particles, Science, 279, 74-76, doi: 10.1126/science.279.5347.74, 1998.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 28973, 2013.