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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.

**Anonymous Referee #2**

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

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.

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.

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?

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."

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.

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

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.

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).

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.

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 ab-



sorption cross-sections were recently revised by IUPAC (in June 2013). Were the most recent values used in this work?

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.

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.

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.

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.

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.

pg 28992, "3.3 Impact on ozone production rate" The model predicts $\sim$10 ppbv of additional 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.

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