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Interactive comment on “An MCM modeling study of nitryl chloride (CINO₂) 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 #1

We thank Referee #1 for their careful reading of the manuscript and comments; below we provide responses to each comment individually.

General Comment by Referee #1:

The paper presents the results of a detailed model analysis of nitryl chloride chemistry

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in polluted continental outflow. This chemistry has been proposed as one of the main activation pathways for chlorine in the troposphere and is certainly a subject that falls within the scope of Atmospheric Chemistry and Physics. The authors discuss in depth the impact of ClNO₂ chemistry on the oxidation processes of VOC, on the formation of ozone and other pollutants (such as acyl peroxy nitrates); interestingly, they also suggest that chlorinated VOC secondary products (such as acid chlorides) may be important Cl sources in polluted regions. The results from this study provide many new insights into our understanding of Cl chemistry and I recommend publication after the authors have addressed a few minor questions.

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

GENERAL AND SPECIFIC COMMENTS

I have a few questions regarding the initialization of the model. Re the scaling of VOC measurements described in Sec 2: was the scaling applied only to ethanol and acetone? From line 11 it seems that all VOC were scaled. If so, it would probably be easier to just use the Atlantis dataset, I think.

**A scaling factor was applied to all of the VOC which showed significant variation between the Atlantis and ground site observations. Ethanol and acetone were simply given as examples of VOC likely influenced by local emissions. Unfortunately, significantly fewer VOC were measured aboard the Atlantis compared to the ground site – 13 vs. 44, respectively (see Supplemental Table S-1). We use the ground site data set in order to constrain the model to the largest number of VOC possible.

Has the aircraft dataset been used at all? It is mentioned only in the introduction of the paper.

**The aircraft data was not used in this study. Using the aircraft measurements to constrain the model in a diurnal sense would be difficult considering that 24-hour fixed type measurements are not feasible given aircraft measurement constraints. We chose

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to mention the aircraft measurements in order to direct readers to other relevant ClNO₂ studies considering that ambient ClNO₂ measurements are still relatively rare.

How were the data from the Atlantis selected? The text only says that the data in the LA region were used, which is bit vague. Were the data filtered for distance from the coast and/or from the ground site?

**We concentrate on the same time period described in Riedel et al. (2012) which we reference in the manuscript. As discussed there Los Angeles outflow region was sampled during the period of May 16 – 31, 2010. We have added this date range to the main text.

How accurate is the assumption of a constant 25C temperature?

**The mean temperature for the ground site was 17 °C with minimums near 13 °C and maximums near 24 °C during the day. While 25 °C is likely an overestimate during the night, it is important to note that we are not trying to explicitly and completely represent the chemistry of the Los Angeles region with the model, only to probe the effects of ClNO₂ formation in regions that might be similar to Los Angeles during the CalNex study – polluted, coastal regions during late spring and early summer. For this purpose we feel that 25 °C represents an appropriate choice. That said we did perform 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% but because the modeled ClNO₂ in this case exceeds that observed, we would need to lower the ClNO₂ yield and thus the actual impact on subsequent daytime chemistry would be negligible. We have added the following statement to the main text to make this clear. “At lower model temperatures a larger fraction of NO_x 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.”

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It would be useful to the community if the authors could make publicly available the expanded CI+VOC mechanism they have developed. Was the MCM protocol, as defined in the Jenkin/Saunders papers, strictly followed (the protocol sets rules on how to exclude minor reaction channels and treat peroxy radicals) or was the mechanism based on the expert judgment of the authors?

**All CI + VOC reactions incorporated into model mechanism and corresponding reaction rate constants have been added 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/>.” For these reaction mechanisms, we relied on our judgment and not the MCM protocol. In general we attempted to be explicit and not simplify. For very fast reactions, such as those of alkoxy radicals we followed the approach specified in Wolfe and Thornton (2011). The following statement clarifying this has been added to the manuscript. “Similar to Wolfe and Thornton (2011), fast reactions, such as the reactions of alkoxy radicals, are treated as instantaneous in order to reduce model stiffness.”

The authors tested the response of the model versus the reaction probabilities of ClONO₂ and HOCl. What about gamma(N₂O₅) and ClNO₂ yield? And the total aerosol surface area?

**We chose to test the model sensitivity to the ClONO₂ and HOCl reaction probabilities because those quantities are more uncertain than gamma(N₂O₅) and the ClNO₂ yield at least for conditions representative a polluted marine region like the Los Angeles outflow. Moreover, for gamma(N₂O₅), the ClNO₂ yield, and total aerosol surface area, we have additional constraints provided by the CalNex field measurements;

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N₂O₅ and ClNO₂ mixing ratios and aerosol surface area concentrations were measured directly during the CalNex study. We focus on reproducing ClNO₂ in excess of 1 ppbv. Therefore the N₂O₅-aerosol reaction probability must be large enough to allow for such ClNO₂ formation. Lowering the N₂O₅-aerosol reaction probability by half, to 0.005, would require a ClNO₂ yield of nearly 100% in order to produce >1 ppbv ClNO₂. Lowering the N₂O₅-aerosol reaction probability to 0.001 or less would result in insufficient ClNO₂ production. For this reason $\gamma(\text{N}_2\text{O}_5) = 0.01$ and a 50% ClNO₂ yield represent a good choice.

It also seems to me that the estimated ClNO₂ photolysis rate as shown in Fig. S7 differs from the observed rate in the period 6-11 am. How sensitive are the results to this parameter?

**The differences between the observed $j\text{ClNO}_2$ and that used by the model, which assumes clear sky conditions and is generally larger than the observed $j\text{ClNO}_2$, would likely result in a slightly shorter ClNO₂ lifetime compared to the observed conditions. While the small differences shown in Supplemental Figure S-7 would not significantly affect the presented results, if the observed $j\text{ClNO}_2$ was used instead, we might expect a slightly slower decay in ClNO₂ throughout the morning and a smaller maximum in Cl atoms.

One of the largest uncertainties in this analysis seems to be HONO. Was it measured at any site during CALNEX and how? How does modelled HONO compares with measured HONO? Heterogeneous HONO formation in the model is mentioned in the summary but not really addressed earlier in the discussion.

**HONO was measured at the CalNex Pasadena ground site via three different techniques. These are described in detail in Young et al. (2012) which we reference frequently in the manuscript. We described the sources and sinks of HONO, in the model, with the statement: "Its abundance otherwise is determined only by the reaction of OH + NO, HONO + OH, and the photolysis of HONO." As one might expect, without a

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heterogeneous HONO source, the model under predicts HONO compared to the observations taken at the ground site. In order to investigate these effects, we constrained the modeled HONO to the measured diurnal profile, and as we describe, we assume that by using these measurements as a constraint any heterogeneous HONO formation reactions are accounted for, and perhaps overestimated because it is not clear that HONO sources in the MBL will be the same as over land. We acknowledge the uncertainty in measured HONO especially regarding differences that might arise between parcels of air over land versus over water in the following statement. "However, as discussed by Young et al. (2012), afternoon and daytime HONO concentrations are fairly uncertain, especially when considering the extent to which HONO measurements over land represent HONO concentrations in the marine boundary layer during morning hours within an air mass that was transported offshore overnight."

TECHNICAL CORRECTIONS

page 28981, line 27: "surface area"

**This change has been made.

page 28990, line 14: "dominates"

**This change has been made.

page 28990, line 16: "sum of"

**This change has been made.

Sources cited:

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