1 Response to Anonymous Referee #1
2
3 We thank Referee #1 for their careful reading of the manuscript and comments; below we provide
4 responses to each comment individually.
5
6 General Comment by Referee #1:
7
8 The paper presents the results of a detailed model analysis of nitryl chloride chemistry in polluted
9 continental outflow. This chemistry has been proposed as one of the main activation pathways for
10 chlorine in the troposphere and is certainly a subject that falls within the scope of Atmospheric
11 Chemistry and Physics. The authors discuss in depth the impact of ClNO2 chemistry on the oxidation
12 processes of VOC, on the formation of ozone and other pollutants (such as acyl peroxy nitrates);
13 interestingly, they also suggest that chlorinated VOC secondary products (such as acid chlorides) may
14 be important Cl sources in polluted regions. The results from this study provide many new insights into
15 our understanding of Cl chemistry and I recommend publication after the authors have addressed a few
16 minor questions.
17
18 Author responses follow each comment and are denoted with **.
19
20
21 GENERAL AND SPECIFIC COMMENTS
22
23 I have a few questions regarding the initialization of the model. Re the scaling of VOC measurements
24 described in Sec 2: was the scaling applied only to ethanol and acetone? From line 11 it seems that all
25 VOC were scaled. If so, it would probably be easier to just use the Atlantis dataset, I think.
26
27 **A scaling factor was applied to all of the VOC which showed significant variation between the
28 Atlantis and ground site observations. Ethanol and acetone were simply given as examples of VOC
29 likely influenced by local emissions. Unfortunately, significantly fewer VOC were measured aboard the
30 Atlantis compared to the ground site – 13 vs. 44, respectively (see Supplemental Table S-1). We use the
31 ground site data set in order to constrain the model to the largest number of VOC possible.
32
33 Has the aircraft dataset been used at all? It is mentioned only in the introduction of the paper.
34
35 **The aircraft data was not used in this study. Using the aircraft measurements to constrain the model in
36 a diurnal sense would be difficult considering that 24-hour fixed type measurements are not feasible
37 given aircraft measurement constraints. We chose to mention the aircraft measurements in order to
38 direct readers to other relevant ClNO2 studies considering that ambient ClNO2 measurements are still
39 relatively rare.
40
41 How were the data from the Atlantis selected? The text only says that the data in the LA region were
42 used, which is bit vague. Were the data filtered for distance from the coast and/or from the ground site?
43
44 **We concentrate on the same time period described in Riedel et al. (2012) which we reference in the
45 manuscript. As discussed there Los Angeles outflow region was sampled during the period of May 16 –
46 31, 2010. We have added this date range to the main text.
47
48 How accurate is the assumption of a constant 25C temperature?
49
50 **The mean temperature for the ground site was 17 °C with minimums near 13 °C and maximums near
51 24 °C during the day. While 25 °C is likely an overestimate during the night, it is important to note that

1

1   we are not trying to explicitly and completely represent the chemistry of the Los Angeles region with
2   the model, only to probe the effects of ClNO2 formation in regions that might be similar to Los Angeles
3   during the CalNex study – polluted, coastal regions during late spring and early summer. For this
4   purpose we feel that 25 °C represents an appropriate choice. That said we did perform a model run for a
5   10 °C case. The lower temperature enhances N2O5 formation given the temperature dependent
6   equilibrium between N2O5, NO3 and NO2. As a result, the maximum in ClNO2 and Cl-atoms increases
7   by ~30% but because the modeled ClNO2 in this case exceeds that observed, we would need to lower
8   the ClNO2 yield and thus the actual impact on subsequent daytime chemistry would be negligible. We
9   have added the following statement to the main text to make this clear. "At lower model temperatures a
10 larger fraction of NOx will react as N2O5 with higher ClNO2 levels and an increased morning Cl·
11 burden relative to warmer cases. This result suggests that we are possibly overestimating the actual yield
12 of ClNO2 per NO2 oxidized by ozone at night."
13
14 It would be useful to the community if the authors could make publicly available the expanded Cl+VOC
15 mechanism they have developed. Was the MCM protocol, as defined in the Jenkin/Saunders papers,
16 strictly followed (the protocol sets rules on how to exclude minor reaction channels and treat peroxy
17 radicals) or was the mechanism based on the expert judgment of the authors?
18
19 **All Cl + VOC reactions incorporated into model mechanism and corresponding reaction rate
20 constants have been added to the supplemental information. The Matlab code containing the additional
21 reactions and rate constants is also now freely available for download at:
22 ftp://ftp.atmos.washington.edu/thornton/UWCM/UWCM_Riedel_etal_rxns.txt
23 We have added the following statement to the manuscript communicating this. "A complete list of the
24 added reactions and reaction rate constants is given in Supplemental Table S-2, and the MATLAB code
25 is freely available for download at ftp://ftp.atmos.washington.edu/thornton/UWCM/." For these reaction
26 mechanisms, we relied on our judgment and not the MCM protocol. In general we attempted to be
27 explicit and not simplify. For very fast reactions, such as those of alkoxy radicals we followed the
28 approach specified in Wolfe and Thornton (2011). The following statement clarifying this has been
29 added to the manuscript. "Similar to Wolfe and Thornton (2011), fast reactions, such as the reactions of
30 alkoxy radicals, are treated as instantaneous in order to reduce model stiffness."
31
32 The authors tested the response of the model versus the reaction probabilities of ClNO3 and HOCl.
33 What about gamma(N2O5) and ClNO2 yield? And the total aerosol surface area?
34
35 **We chose to test the model sensitivity to the ClONO2 and HOCl reaction probabilities because those
36 quantities are more uncertain than gamma(N2O5) and the ClNO2 yield at least for conditions
37 representative a polluted marine region like the Los Angeles outflow. Moreover, for gamma(N2O5), the
38 ClNO2 yield, and total aerosol surface area, we have additional constraints provided by the CalNex field
39 measurements; N2O5 and ClNO2 mixing ratios and aerosol surface area concentrations were measured
40 directly during the CalNex study. We focus on reproducing ClNO2 in excess of 1 ppbv. Therefore the
41 N2O5-aerosol reaction probability must be large enough to allow for such ClNO2 formation. Lowering
42 the N2O5-aerosol reaction probability by half, to 0.005, would require a ClNO2 yield of nearly 100% in
43 order to produce >1 ppbv ClNO2. Lowering the N2O5-aerosol reaction probability to 0.001 or less
44 would result in insufficient ClNO2 production.
45 For this reason gamma(N2O5) = 0.01 and a 50% ClNO2 yield represent a good choice.
46
47 It also seems to me that the estimated ClNO2 photolysis rate as shown in Fig. S7 differs from the
48 observed rate in the period 6-11 am. How sensitive are the results to this parameter?
49
50 **The differences between the observed jClNO2 and that used by the model, which assumes clear sky
51 conditions and is generally larger than the observed jClNO2, would likely result in a slightly shorter

2

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 jClNO2 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 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:

Riedel, T. P., Bertram, T. H., Crisp, T. A., Williams, E. J., Lerner, B. M., Vlasenko, A., Li, S.-M., Gilman, J., de Gouw, J., Bon, D. M., Wagner, N. L., Brown, S. S., and Thornton, J. A.: Nitryl Chloride and Molecular Chlorine in the Coastal Marine Boundary Layer, Environmental Science & Technology, 46, 10463-10470, doi: 10.1021/es204632r, 2012.

1   Wolfe, G. M., and Thornton, J. A.: The Chemistry of Atmosphere-Forest Exchange (CAFE) Model –
2   Part 1: Model description and characterization, Atmos. Chem. Phys., 11, 77-101, doi: 10.5194/acp-11-
3   77-2011, 2011.
4
5   Young, C. J., Washenfelder, R. A., Roberts, J. M., Mielke, L. H., Osthoff, H. D., Tsai, C., Pikelnaya, O.,
6   Stutz, J., Veres, P. R., Cochran, A. K., VandenBoer, T. C., Flynn, J., Grossberg, N., Haman, C. L.,
7   Lefer, B., Stark, H., Graus, M., de Gouw, J., Gilman, J. B., Kuster, W. C., and Brown, S. S.: Vertically
8   Resolved Measurements of Nighttime Radical Reservoirs; in Los Angeles and Their Contribution to the
9   Urban Radical Budget, Environmental Science & Technology, 46, 10965-10973, doi:
10   10.1021/es302206a, 2012.
11
12

1 Response to Anonymous Referee #2
2
3 We thank Referee #2 for their careful reading of the manuscript and comments; below we provide
4 responses to each comment individually.
5
6 General Comment by Referee #2:
7
8 Riedel et al. report the addition of chlorine chemistry to the Master Chemical Mechanism and apply the
9 new mechanism to data collected during the Calnex-LA 2010 field campaign (focusing on the L.A.
10 urban outflow). The new mechanism allowed the identification and prediction of concentrations of
11 several halogenated VOCs produced during the Cl initiated oxidation of alkenes and of the nature and
12 abundances of organic peroxy radicals produced. The authors confirm that the nocturnal conversion of
13 N2O5 to ClNO2 and subsequent ClNO2 photolysis increases O3 production on the following day in the
14 study region. The authors also show that about 3/4 of the Cl produced by morning ClNO2 photolysis
15 converts to HCl, and that the remainder converts to ClO (via reaction of Cl with O3) or forms
16 organochlorine molecules (via reaction of Cl with unsaturated hydrocarbons). Overall, the paper is
17 written well, is thorough, and presents important results that should be published after my minor
18 concerns below have been addressed.
19
20 Author responses follow each comment and are denoted with **.
21
22
23 General comments
24
25 1. The methodology used needs to be described in more detail. The additions are partly described on pg
26 28982 and in the supplement, but the paper is lacking a comprehensive table listing all of the reactions
27 and rate coefficients that have been added to the model. Perhaps better still: Have the authors considered
28 including the new MCM code as an appendix to this paper, or making it available for download on a
29 web site or ftp server? After all, a considerable portion of this work is based on what was made freely
30 available for download at the Leeds web site, and it would be a great service to the community if the
31 authors were to follow the spirit of the MCM creators in this regard.
32
33 **We have added a table outlining all of the additional chlorine reactions and used rate constants not
34 present in the native MCM to the supplemental information. The Matlab code containing the additional
35 reactions and rate constants is also now freely available for download at:
36 ftp://ftp.atmos.washington.edu/thornton/UWCM/UWCM_Riedel_etal_rxns.txt. We have added the
37 following statement to the manuscript communicating this. "A complete list of the added reactions and
38 reaction rate constants is given in Supplemental Table S-2, and the MATLAB code is freely available
39 for download at ftp://ftp.atmos.washington.edu/thornton/UWCM/."
40
41 2. Calculated quantities were not compared with actual measurements. As such, the authors combined
42 data from different measurement locations that are quite distant from each other. I agree that this was
43 necessary to compensate for lack of certain measurements on the Atlantis. However, many of the
44 estimated species used as model inputs and some of the species calculated (e.g., OH, HO2) were
45 measured at the ground site. It would have made for a stronger and perhaps more interesting paper if the
46 model presented here had been applied to and compared with measurements at the ground site only
47 rather than to a mixed ship/ground site data set. Perhaps something that could be considered for a future
48 paper.
49
50 **It is true that the majority of modeling papers focus on comparing model outputs to field
51 measurements with an emphasis on reproducing the observations. However, in this study we did not

5

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 ClNO¬2 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.

6

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 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.

**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.

An MCM modeling study of nitryl chloride (ClNO$_2$) impacts on oxidation, ozone production and nitrogen oxide partitioning in polluted continental outflow

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Abstract

Nitryl chloride ($ClNO_2$) is produced at night by reactions of dinitrogen pentoxide (N_2O_5) on chloride containing surfaces. $ClNO_2$ is photolyzed during the morning hours after sunrise to liberate highly reactive chlorine atoms (Cl·). This chemistry takes place primarily in polluted environments where the concentrations of N_2O_5 precursors (nitrogen oxide radicals and ozone) are high, though it likely occurs in remote regions at lower intensities. Recent field measurements have illustrated the potential importance of $ClNO_2$ as a daytime Cl· source and a nighttime NO_x reservoir. However, the fate of the Cl· and the overall impact of $ClNO_2$ on regional photochemistry remain ~~unclear~~ poorly constrained by measurements and models. To this end, we have incorporated $ClNO_2$ production, photolysis, and subsequent Cl· reactions into an existing Master Chemical Mechanism (MCM version 3.2) box model framework using observational constraints from the CalNex 2010 field study. Cl· reactions with a set of alkenes and alcohols, and the simplified multiphase chemistry of N_2O_5, $ClNO_2$, $HOCl$, $ClONO_2$, and Cl_2, none of which are currently part of the MCM, have been added to the mechanism. The presence of $ClNO_2$ produces significant changes to oxidants, ozone, and nitrogen oxide partitioning, relative to model runs excluding $ClNO_2$ formation. From a nighttime maximum of 1.5 ppbv $ClNO_2$, the daytime maximum Cl· concentration reaches 1×10^5 atoms cm^{-3} at 7 AM, reacting mostly with a large suite of volatile organic compounds (VOC) to produce 2.2 times more organic peroxy radicals in the morning than in the absence of $ClNO_2$. In the presence of several ppbv of nitrogen oxide radicals ($NO_x = NO + NO_2$), these perturbations lead to similar enhancements in hydrogen oxide radicals ($HO_x = OH + HO_2$). Neglecting contributions from HONO, the total integrated daytime radical source is 17% larger when including $ClNO_2$, which leads to a similar enhancement in integrated ozone production of 15%. Detectable levels (tens of pptv) of chlorine containing organic compounds are predicted to form as a result of Cl· addition to alkenes, which may be useful in identifying times of active Cl· chemistry.
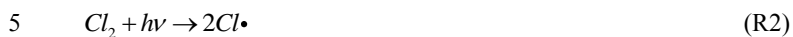
1   Introduction

Chlorine atoms (Cl·) are highly reactive, often having rate constants for reactions with volatile organic compounds (VOC) that are factors of 10 to 200 larger than the hydroxyl radical, OH, which is considered the atmosphere's primary initiator of oxidation. As a result, the presence of Cl· can lead to shorter lifetimes for VOC and an enhanced radical pool which can potentially enhance the production of ozone in polluted areas. The global tropospheric Cl· budget remains uncertain, with a large range in recent studies (~15 – 40 Tg Cl yr^{-1}) developed from indirect means (Allan et al., 2007; Platt et al., 2004)

1 as tropospheric Cl· concentrations are not presently measurable by existing methods. There are a

2 number of potential Cl· sources in the troposphere, the major sources are outlined in Reactions R1 – R5.

3

4 $HCl + OH \rightarrow Cl\bullet + H_2O$ (R1)

5 $Cl_2 + h\nu \rightarrow 2Cl\bullet$ (R2)

6 $BrCl + h\nu \rightarrow Cl\bullet + Br\bullet$ (R3)

7 $ClNO + h\nu \rightarrow Cl\bullet + NO$ (R4)

8 $ClNO_2 + h\nu \rightarrow Cl\bullet + NO_2$ (R5)

9

10 The reaction of hydrochloric acid (HCl) with the hydroxyl radical (OH) is a daytime source of Cl·.

11 Typical HCl mixing ratios in the troposphere vary from 100 – 5000 pptv with the highest found in

12 polluted regions with direct HCl emissions from industrial processes and acid displacement of aqueous

13 chloride by HNO_3 and H_2SO_4 (Keene et al., 2007). Cl· formed by HCl + OH tend to peak around

14 midday with the peak in OH formed from $O(^1D) + H_2O$. Additionally, the oxidation of many VOC by

15 Cl· proceeds via a hydrogen abstraction to form HCl, thus recycling this Cl· source.

16

17 Photolysis of molecular chlorine (Cl_2) produces two Cl· and has been the focus of many Cl·

18 investigations since it was first measured at elevated concentrations in ambient air (Finley and

19 Saltzman, 2006, 2008; Lawler et al., 2011; Riedel et al., 2012a; Spicer et al., 1998). Cl_2 mixing ratios

20 were often on the order of tens of pptv with maximum reported mixing ratios near 100 – 200 pptv.

21 Direct Cl_2 emissions are related to power generation, water treatment, and oil refineries (Sarwar and

22 Bhave, 2007). Recently, a low pH Cl_2 production channel that may be atmospherically relevant has been

23 identified in the reaction of N_2O_5 with chloride containing substrates, which involved $ClNO_2$ as an

24 intermediate (Roberts et al., 2008). In addition, Cl_2 can be formed in situ through multiphase chemistry

25 involving chlorine nitrate ($ClONO_2$) and hypochlorous acid (HOCl). These species, in turn, can

26 photolyze to reform Cl· or ClO or react on acidic, chloride-containing particles to form Cl_2. In polluted

27 air, the reaction of ClO with NO, which completes a null cycle producing Cl· and NO_2, limits the

28 potential for multiphase Cl_2 formation.

29

30 BrCl photolysis to form Cl· and atomic bromine is also thought to be an important Cl· source, especially

31 in remote regions. In polar regions, BrCl mixing ratios on the order of tens of pptv have been measured

32 (Buys et al., 2013; Foster et al., 2001; Spicer et al., 2002). To our knowledge there have been no

33 reported observations of BrCl in ambient air outside of polar regions (Finley and Saltzman, 2008). BrCl
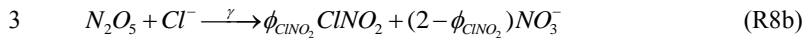
can form through heterogeneous reactions of $BrONO_2$ and $HOBr$ on acidic, chloride-containing particles in an analogous manner to the Cl_2 formation reactions described above or through reactions of $ClONO_2$ and $HOCl$ on acidic, bromide-containing particles.

Nitrosyl chloride (ClNO) has also been proposed as a potential Cl· source (Raff et al., 2009). These theoretical and laboratory studies have yet to be confirmed by field measurements of ClNO in ambient air. Using a regional 3-D chemical transport model, Raff et al. predict that ClNO mixing ratios in polluted marine areas could reach ppbv values. That said, the hydrolysis of ClNO at moderate and high relative humidity (RH>20%) will likely be sufficiently rapid to prevent the buildup of appreciable atmospheric concentrations of ClNO (Karlsson and Ljungström, 1996; Rubasinghege and Grassian, 2012; Scheer et al., 1997).

Since its proposed atmospheric formation by Finlayson-Pitts et al. (1989) and first observation in ambient air by Osthoff et al. (2008), nitryl chloride ($ClNO_2$) has been observed during a number of different field studies worldwide with nighttime maximum mixing ratios ranging from tens of pptv to over 2 ppbv (Kercher et al., 2009; Mielke et al., 2011; Mielke et al., 2013; Osthoff et al., 2008; Phillips et al., 2012; Riedel et al., 2012a; Thornton et al., 2010; Young et al., 2012). These observations have occurred in both continental and marine locations illustrating the importance of $ClNO_2$ as a Cl· source in a variety of different environments. $ClNO_2$ represents a Cl· source with clear anthropogenic origins as it is formed at night by reactions involving NO_x (NO_2 + NO), ozone, and chloride containing aerosols. Anthropogenic activities associated with power generation, motor vehicle use, and agriculture now dominate the global NO_x source (Jaegle et al., 2005). Natural sources of NO_x, such as microbial activity, lightning, and wildfires, are also significant globally, but the impact of these NO_x sources on $ClNO_2$ formation remain unknown. At night, a fraction of NO_x is converted into $ClNO_2$ through Reactions R6 – R8. The branching ratio between Reactions R8a and R8b, commonly referred to as the $ClNO_2$ yield (ϕ_{ClNO_2}), is determined by the efficiency of $ClNO_2$ formation from heterogeneous reactions of N_2O_5. The ϕ_{ClNO_2} and the N_2O_5-particle reaction probability, $\gamma(N_2O_5)$, are uncertain quantities that can vary significantly depending on a number of factors such as particulate water, chloride, nitrate, and organic content (Badger et al., 2006; Bertram and Thornton, 2009; McNeill et al., 2006; Mentel et al., 1999; Thornton et al., 2003). After sunrise, the photolysis of $ClNO_2$ produces Cl· and NO_2, thereby partially circumventing the removal of NO_x through the formation and loss of $2HNO_3$ (R8a).

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \qquad\qquad\qquad\qquad (R6)$$

Comment [TPR1]: Added Mielke et al., 2013 reference.

12

1      $NO_3 + NO_2 \leftrightarrow N_2O_5$ (R7)

2      $N_2O_5 + H_2O \xrightarrow{\gamma} 2HNO_3$ (R8a)

3      $N_2O_5 + Cl^- \xrightarrow{\gamma} \phi_{ClNO_2} ClNO_2 + (2 - \phi_{ClNO_2})NO_3^-$ (R8b)
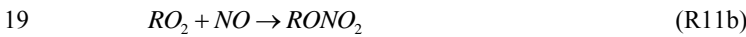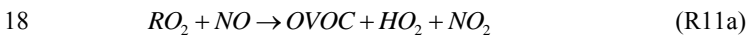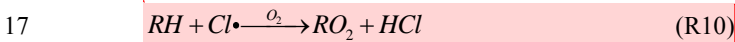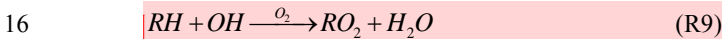
4

5   The Cl· budget, hydrogen oxide and organic peroxy radical abundance (RO_x = OH + HO_2 + RO_2), NO_x

6   lifetime and partitioning among other forms of reactive nitrogen, and the net ozone production rate are

7   linked through photochemical oxidation of VOC. As shown in Reactions R9 – R12 the oxidation of a

8   hydrocarbon (RH) is initiated by reaction with OH or Cl· to form the organic peroxy radical (RO_2). In

9   polluted regions, the dominant fate of RO_2 is to react with NO. The dominant channel of this reaction

10   eventually leads to a closed shell oxygenated hydrocarbon (OVOC – oxygenated volatile organic

11   compound), hydroperoxyl radical (HO_2) and NO_2, while the minor channel leads to an alkyl nitrate

12   ($RONO_2$). If the RO_2 is an acyl peroxy radical, then reaction with NO_2 produces acyl peroxy nitrates

13   (APN) such as acetyl peroxy nitrate (PAN). NO also reacts with HO_2 to form NO_2 and OH. Through

14   these reactions ozone is produced from the photolysis of NO_2.

15

16     $RH + OH \xrightarrow{O_2} RO_2 + H_2O$ (R9)

17     $RH + Cl\bullet \xrightarrow{O_2} RO_2 + HCl$ (R10)

18     $RO_2 + NO \rightarrow OVOC + HO_2 + NO_2$ (R11a)

19     $RO_2 + NO \rightarrow RONO_2$ (R11b)

20     $RO_2 + NO_2 \leftrightarrow APN$ (R12)

21

22   From the above discussion, we expect that $ClNO_2$ acts similarly, though not exactly the same, as an OH

23   source such as that from nitrous acid (HONO) photolysis or $O(^1D)$ + H_2O. When the radical pool is

24   terminated via cross reactions between RO_x and NO_x, a higher production rate of HO_x or Cl· will nearly

25   linearly increase the ozone production rate (Daum et al., 2000; Kleinman, 2005). Moreover, at high NO,

26   production of an RO_2 by Cl· attack directly increases the steady state concentration of OH and HO_2 due

27   to the rapid cycling between OH, HO_2 and RO_2. However, the increased RO_2 due to Cl· arises from a

28   potentially different pool of hydrocarbons than that from OH, given the large differences in RH

29   abundance and relative reactivity towards OH and Cl·. Moreover, $ClNO_2$ photolysis predominantly

30   occurs in the first few hours after sunrise, well before the maximum OH production rate from $O(^1D)$ +

31   H_2O and before the maximum in NO/NO_2. Thus, the full impact of $ClNO_2$ on ozone production, VOC

Comment [TPR2]: Added O2 above reaction arrow.

1 lifetime and NO_x abundance and partitioning may not be the same as simply scaling the daytime average

2 HO_x production rate.

3

4 Here we examine the effects of $ClNO_2$ formation as predicted by a detailed box model that incorporates

5 the Master Chemical Mechanism and is constrained by ground and ship-based ambient measurements

6 taken during the CalNex 2010 field study. The aim is not to replicate specific observations or

7 conditions, but rather to use the model to develop conceptual insights into the effect of a morning pulse

8 of chlorine atoms in polluted air. We use the model to assess the impact of $ClNO_2$ on the Cl· budget,

9 RO_x abundance, NO_x lifetime and partitioning, and the net ozone production rate.

10

11 **2   Measurements and model description**

12

13 We chose to constrain a box model using data taken during the CalNex field study, which occurred in

14 May and June of 2010 in the southern California region (Ryerson et al., 2013). The goal of these

15 modeling studies is not to replicate the evolution of specific air masses in the LA Basin, but instead to

16 more generally probe the effect of multiphase reactive nitrogen and reactive halogen chemistry on

17 radical budgets, ozone production, and the fate of NO_x in polluted coastal regions. There were multiple

18 measurement platforms involved in CalNex, three of which recorded both $ClNO_2$ and extensive VOC

19 measurements: the Research Vessel *Atlantis*, a ground site located on the California Institute of

20 Technology campus in Pasadena, CA, and aircraft measurements taken on the NOAA WP-3D (Mielke

21 et al., 2013; Riedel et al., 2012a; Young et al., 2012). Though the R/V *Atlantis* sampled in many

22 locations along the southern California coast, we focus on the measurements made in and around Los

23 Angeles urban outflow due to the added constraints provided by the Pasadena ground site

24 measurements. $ClNO_2$ mixing ratios in the nocturnal outflow from the Los Angeles region were

25 commonly over 500 pptv with maximums on the order of 2 ppbv (Riedel et al., 2012a; Wagner et al.,

26 2012).

27

28 Cl· chemistry was incorporated into an existing model framework described in Wolfe and Thornton

29 (2011) which is based on the Master Chemical Mechanism version 3.2 (MCM) developed at the

30 University of Leeds (more information available at http://mcm.leeds.ac.uk/MCM) (Bloss et al., 2005;

31 Jenkin et al., 1997; Jenkin et al., 2003; Saunders et al., 2003). Use of the MCM allows for explicit

32 tracking of approximately 2800 chemical species and about 9000 different reactions with reaction rate

33 constants derived from the International Union of Pure and Applied Chemistry (IUPAC) kinetics

34 database (http://www.iupac-kinetic.ch.cam.ac.uk). Similar to Wolfe and Thornton (2011), fast reactions,

14

Comment [TPR3]: Added references.

such as reactions of alkoxy radicals, are treated as instantaneous in order to reduce model stiffness.

In total, 44 of the VOC measured at the Pasadena site are used to constrain the model. However, certain VOC, for example ethanol (median value = 8.2 ppbv) and acetone (median value = 3.8 ppbv), measured at the Pasadena ground site appeared to often be dominated by highly localized emissions. To more generally represent an urban air mass in the model, ground site VOC measurements were scaled by those measured on the R/V *Atlantis*. A smaller number of VOC were measured aboard the R/V *Atlantis*, so species not represented in the R/V *Atlantis* dataset were scaled by species of similar structure (i.e., similar functional groups). For example, methanol was measured with median levels of approximately 6 ppbv and 1 ppbv at the ground site and on the ship, respectively. Ethanol, however, was only measured at the ground site. To estimate ethanol levels in the urban outflow and be more representative of what the R/V *Atlantis* might have sampled, the ground site ethanol mixing ratios were simply scaled down by 1/6. For a complete list of the measured VOC used in the model see Supplemental Information Table S-1.

VOC and HCl mixing ratios are held to their ship-scaled hourly average diurnal profiles for a 69 hour "spin-up" period. The diurnal HCl profile used is shown in Supplemental Figure S-1. NO_2, O_3, and CO are held to mean values measured at the ground site during this spin-up period. In addition, we fix methane at a mixing ratio of 1.8 ppmv. Over the entirety of a model run temperature is held constant at 25 °C and the aerosol surface area concentration is held constant at 350 μm^2 cm^{-3}, which represents some of the largest aerosol surface area concentrations encountered by the R/V *Atlantis* while sampling Los Angeles outflow. At lower model temperatures a larger fraction of NO_x will react as N_2O_5 with higher $ClNO_2$ levels and an increased morning Cl· burden relative to warmer cases. This result suggests that we are possibly overestimating the actual yield of $ClNO_2$ per NO_2 oxidized by ozone at night. The box model does not attempt to replicate the effects of meteorology and thus the processes of dilution and deposition are not accurately incorporated. To maintain reasonable concentrations of the many modeled species which were not constrained by observations, we apply a continuous dilution rate of 1.5% per hour to all species. Formaldehyde and nitric acid have an additional deposition rate of 30% per hour in order to keep mixing ratios at levels most similar to those sampled during the CalNex study (<6 ppbv for formaldehyde) (Warneke et al., 2011). The sensitivity of the results to this additional loss rate is minor (<20% adjustments to the Cl· budget), and the need for this additional loss is likely related to our neglect of deposition for intermediate organic oxidation products (in the case of formaldehyde) and of HNO_3 itself. Isoprene, alpha-pinene, beta-pinene, and limonene are allowed to freely evolve at night during the spin-up period to avoid unrealistic conditions whereby NO_3 reactions with these compounds
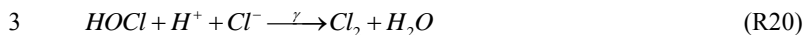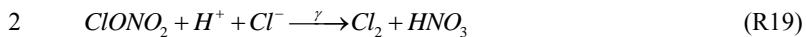
15

proceeded indefinitely throughout the night. That is, we assume that advection of air masses from the land out over the water (either at the surface or aloft of the continental nocturnal surface layer) would ultimately limit the source of reactive biogenic VOC. At hour 69, which represents sunset on the third model day, all species are released from observational constraints and the chemistry evolves freely for another 27 hours. We use the final 24-hours of a model run as the analysis period. All figures and calculations described here are performed on the model output from this period.

A number of reactions necessary for evaluating Cl· production and reactivity are not included in the MCM. Version 3.2 of the MCM only includes Cl· reactions with alkanes. In order to accurately represent the chemistry, multiple mechanisms were added to the model framework. These include the Reactions R1 – R3, R8, R13 – R21, and a number of VOC + Cl· reactions such as those for methanol, ethanol, isopropanol, ethene, propene, formaldehyde, ethanal, propanal, acetone, benzene, styrene, o-xylene, toluene. Several of the added mechanisms are explicitly shown in the Supplemental Information (Supplemental Figure S-2 – S-6). 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/. The reaction rate constants and product branching for these reactions were taken from the IUPAC kinetics database as of May 11, 2012. Chlorinated products not present in the MCM or available in the IUPAC database were assumed to react similarly and with similar rate constants to non-chlorinated species of the same structure already in the MCM (see Supplemental Table S-2). Additionally, our revised mechanism explicitly tracks gas-phase HCl formation that results from hydrogen atom abstraction reactions by Cl. $ClNO_2$ photolysis frequencies were estimated by scaling measured NO_2 photolysis frequencies down by a factor of 30 (i.e., $j_{NO_2}/30$). This approximation produces $ClNO_2$ photolysis frequencies close to observations taken aboard the R/V *Atlantis* (Supplemental Figure S-7). Photolysis frequencies for Cl_2, $ClONO_2$, and HOCl were calculated using the Tropospheric Ultraviolet and Visible (TUV) Radiation Model (available at http://cprm.acd.ucar.edu/Models/TUV) and incorporated into the box model.

$$Cl\cdot + O_3 \rightarrow ClO + O_2 \qquad (R13)$$

$$ClO + NO_2 \rightarrow ClONO_2 \qquad (R14)$$

$$ClO + HO_2 \rightarrow HOCl + O_2 \qquad (R15)$$

$$ClONO_2 + h\nu \rightarrow Cl\cdot + NO_3 \qquad (R16)$$

$$ClONO_2 + h\nu \rightarrow ClO + NO_2 \qquad (R17)$$

1	$HOCl + h\nu \rightarrow Cl\bullet + OH$	(R18)
2	$ClONO_2 + H^+ + Cl^- \xrightarrow{\gamma} Cl_2 + HNO_3$	(R19)
3	$HOCl + H^+ + Cl^- \xrightarrow{\gamma} Cl_2 + H_2O$	(R20)
4	$ClO + NO \rightarrow Cl\bullet + NO_2$	(R21)

5

6　For alkenes, the major pathway involves addition of chlorine to the double bond rather than the typical

7　hydrogen abstraction pathway (Atkinson et al., 2004). This pathway leads to chlorinated products which

8　might be detectable as tracers of Cl· chemistry in future studies. As we show below, such compounds

9　could be another avenue for Cl· recycling. Reactions of Cl· with isoprene, which also produces unique

10　chlorinated products, were not included in the model framework given its modest <1% contribution to

11　total Cl· reactivity in the modeled Los Angeles outflow and the large increase in complexity when

12　incorporating the mechanism (Fan and Zhang, 2004; Tanaka et al., 2003). Instead, the products of Cl· +

13　isoprene were tracked as a single generic species with no chemical losses. However, in areas where

14　isoprene is a more significant contributor to Cl· reactivity, it would be necessary to include a more

15　explicit isoprene oxidation mechanism to accurately capture the effects Cl·, especially to assess any

16　chlorinated products that might form from these reactions (Riemer et al., 2008). In such locations the

17　products of chlorine-initiated isoprene oxidation are likely more pronounced than in the Los Angeles

18　region.

19

20　Gas-particle reaction probabilities in the model are set to 0.01 for N_2O_5, $ClONO_2$, and HOCl (R8, R19,

21　R20). A $\gamma = 0.01$ is within the typical range of $\gamma(N_2O_5)$ measured on ambient aerosol (<0.001 – 0.03) at

22　elevated RH during various field studies (Bertram et al., 2009; Riedel et al., 2012b). Laboratory

23　measurements of $ClONO_2$ and HOCl uptake under stratospheric and tropospheric conditions on sulfuric

24　acid, sodium chloride, and sodium bromide particles and pure water droplets generally report γ values

25　<0.06 for $ClONO_2$ and HOCl (Deiber et al., 2004; Hanson and Ravishankara, 1994; Hanson et al.,

26　1994). We make the upper-limit assumption that reactions of $ClONO_2$ and HOCl on aerosol particles

27　produce only Cl_2 with unit efficiency. Given that Cl_2 production from heterogeneous reactions of

28　$ClONO_2$ and HOCl is proportional to the product of γ and the yield, we use $\gamma = 0.01$ and a 100% yield

29　on all particles in the model.

30

31　To examine the effects of $ClNO_2$ formation, we vary ϕ_{ClNO_2} between 0% and 50% in successive model

32　runs, which produce a without-$ClNO_2$ case and a with-$ClNO_2$ case, respectively. A 50% yield results in

33　~1.5 ppbv of $ClNO_2$ as shown in Figure 1, which is similar to levels in the Los Angeles outflow

17

1 conditions encountered during CalNex. We also performed a series of model runs where HONO was

2 constrained to observations made at the Pasadena ground site. Its abundance otherwise is determined

3 only by the reaction of OH + NO, HONO + OH, and the photolysis of HONO. Most of our main

4 conclusions reported here are relatively insensitive to HONO. Moreover, the vertical profiles of $ClNO_2$

5 and HONO throughout the nocturnal and evolving daytime boundary layer are likely different (Young et

6 al., 2012), making our primary focus on $ClNO_2$ a reasonable simplification for a box model.

7

8 **3   Results and discussion**

9

10 *3.1 Cl-atom budget*

11

12 The model predicts that, integrated over a typical day in the Los Angeles outflow, $ClNO_2$ is the major

13 driver of Cl· evolution. Neither HCl + OH nor multiphase chemistry involving $ClONO_2$ and HOCl to

14 produce Cl_2 are competitive with the $ClNO_2$ source. Moreover, this picture is consistent with that

15 derived solely from observations in this region (Riedel et al., 2012a). Figure 1 shows the Cl·

16 concentration predicted by the model during the 24-hour analysis period for both the with-$ClNO_2$ and

17 without-$ClNO_2$ cases. When $ClNO_2$ formation is included, the Cl· concentration reaches a maximum at

18 ~7 AM (2 hours after model sunrise) with a value of 1.08×10^5 atoms cm^{-3}. A substantially different

19 picture results from the without-$ClNO_2$ case where the maximum Cl· concentration occurs around noon

20 and only reaches 0.2×10^5 atoms cm^{-3}. The assumptions made about the aerosol reaction probabilities of

21 $ClONO_2$ and HOCl partially drive the late afternoon Cl· profile, which, as a result, is more uncertain.

22 However, this afternoon Cl· concentration profile is not especially sensitive to the assumed reaction

23 probabilities. For example, increasing the reaction probabilities of $ClONO_2$ and HOCl from 0.01 to 0.1

24 does not substantially change the 24-hour profile. The maximum in Cl· concentration is increased by

25 ~10% still occurring in the early morning hours after sunrise (~7 AM), and the integrated Cl·

26 concentration over the entire day is enhanced by only 20%. Additionally, the choice of 0.01 for a

27 $ClONO_2$ and HOCl reaction probability and a 100% Cl_2 yield is likely more realistic as the formation of

28 Cl_2 from these reactions is unlikely to be the sole product (Caloz et al., 1996; Santschi and Rossi, 2005).

29 That said, to fully understand the impact of Cl· chemistry in coastal urban areas, the fate of $ClONO_2$

30 especially needs to be better constrained.

31

32 The evolution of Cl· largely follows that of the dominant source terms, as shown in Figure 2. In the

33 absence of $ClNO_2$ formation (Fig. 2A), the bulk of Cl· production results from the HCl + OH production

34 channel, and the maximum in Cl· production rate of 0.5×10^6 atoms cm^{-3} s^{-1} coincides with the maximum

18

production from the HCl + OH channel. In the with-ClNO$_2$ case (Fig. 2B), the maximum Cl· production rate occurs at 7 AM with a value of 3.4×10^6 atoms cm^{-3} s^{-1} corresponding to the maximum contribution from ClNO$_2$ photolysis. The ClNO$_2$ production channel represents 56% of Cl· production over the course of the entire day, leading to nearly 3.7 times as many Cl· produced relative to the without-ClNO$_2$ case. By noon, ClNO$_2$ is largely depleted under the clear-sky model conditions, and other Cl· production channels like the reaction of HCl with OH and the photolysis of Cl$_2$ from HOCl and ClONO$_2$ heterogeneous chemistry become more dominant. These production channels involving multi-phase Cl-recycling to form Cl$_2$ show significant enhancements when ClNO$_2$ formation is included. For example, Cl· production from ClONO$_2$ photolysis, HOCl photolysis, and Cl$_2$ photolysis are enhanced by factors of 3.3, 2.2, and 3.3, respectively over the without-ClNO$_2$ case. To some extent these enhancements should be expected considering the larger Cl· pool available for recycling reactions when ClNO$_2$ formation is allowed, but they give indication of the degree of indirect coupling between ClNO$_2$ and Cl$_2$ via the increased formation of reactive chlorine reservoirs like ClONO$_2$ and HOCl. During CalNex, molecular chlorine was also measured along with ClNO$_2$ (Riedel et al., 2012a). Observations of nighttime and early morning Cl$_2$ were typically in the 5 – 50 pptv range. Modeled Cl$_2$ levels are of similar magnitude to these observations, as well as previous observations of Cl$_2$ in this region (Finley and Saltzman, 2006, 2008), and show a morning enhancement with slightly elevated levels throughout the day but only with the inclusion of ClNO$_2$ (see Supplemental Figure S-8). For additional information on the model concentrations of the Cl· source species see Supplemental Figure S-9.

Given the lack of BrCl observations outside of polar regions, we do not include BrCl formation in the model and therefore do not explicitly account for the potential Cl· source, if any, represented by BrCl. Considering Cl$_2$ represents 16% of the integrated Cl· source over the course of a model day, the typical seawater ratio of chloride to bromide of ~650:1, and assuming that BrCl formation is not significantly faster than 650 times Cl$_2$ formation, we estimate an upper limit Cl· source from BrCl resulting from ClONO$_2$ and HOCl reactions that is similar to that predicted from Cl$_2$. That said, BrCl formed from these reactions should not significantly bias our Cl· estimates considering that we force these reactants to produce exclusively Cl$_2$, the photolysis of which forms 2Cl· compared to only 1Cl· from BrCl photolysis. However, heterogeneous reactions of BrONO$_2$ and HOBr to form BrCl are not accounted for at all. Using maximum HCl levels as a measure of particulate chloride displaced over Los Angeles and the expected chloride to bromide ratio in seawater, 2.5 ppbv of chloride corresponds to ~4 pptv of bromide available for BrCl formation. Incorporating this amount of total bromine into the model and assuming γ(BrONO$_2$) and γ(HOBr) = 0.1 with a unit yield of BrCl, we predict the model could be neglecting a Cl· source from BrCl on the order of 5% of the Cl· concentration integrated over the model

19

day. Ambient measurements of BrCl in polluted coastal regions would be a particularly useful constraint on the extent of these $Cl\cdot$ recycling reactions and the role of bromide.

The use of a comprehensive chemical mechanism such as the MCM also illustrates a potentially important but heretofore overlooked source of $Cl\cdot$ in polluted regions. In the with-$ClNO_2$ case, the reaction of OH with formyl chloride (CHOCl), produced from $Cl\cdot$ attack of alkenes, becomes a noticeable $Cl\cdot$ source during the afternoon. Interestingly, CHOCl photolysis is predicted to be a $Cl\cdot$ source comparable in magnitude to that from HOCl photolysis (Figure 2B). In fact, because we possibly overestimate the actual multi-phase recycling of $ClONO_2$ and HOCl to form Cl_2, $Cl\cdot$ release from such acid chlorides may be more important than these multiphase processes in regions with significant alkene concentrations. This result suggests observations of acid chlorides would be as beneficial as Cl_2 in polluted regions.

HONO has a noticeable impact on the afternoon $Cl\cdot$ budget via photolysis to form OH followed by the reaction of OH + HCl. Constraining the model to the HONO diurnal profile measured at the Pasadena ground site leads to a 60% increase (1.4×10^7 to 2.26×10^7 molecules cm^{-3}) in the daily maximum OH concentration and a similar increase in the integrated $Cl\cdot$ formation rate from OH + HCl. Multiphase recycling via $ClONO_2$ and HOCl are also increased as a result of the larger $Cl\cdot$ concentrations. 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.

We also investigate the formation potential of chlorinated products at potentially detectable quantities resulting from the $Cl\cdot$ oxidation of VOC. These species could represent "tracers" of $Cl\cdot$ chemistry and indicate the extent to which $Cl\cdot$ oxidation reactions are occurring. This issue has been investigated previously in the Houston area using ground based measurements of potential products from $Cl\cdot$ oxidation of isoprene (Riemer et al., 2008). As stated above, chlorinated products of $Cl\cdot$ reactions with isoprene are not included our model and are likely of minor importance to total $Cl\cdot$ reactivity in the Los Angeles region. Within our model framework, $Cl\cdot$ addition reactions with ethene and propene can produce chlorinated products such as 2-chloroperoxypropionyl nitrate (2-chloroPPN), chloroacetaldehyde, 2-chloroperoxyacetyl nitrate (2-chloroPAN), formyl chloride, 2-chloropropanal, and chloroacetone – some of which have been previously investigated in polar regions (Keil and Shepson, 2006). As with most of the previously mentioned effects, these enhancements are pronounced

20

in the early part of the day when Cl· and VOC concentrations are highest in the model. As we show in Figure 3, morning enhancements are typically on the order of 5-30 pptv above the background generated during the spin-up period. Chloroacetaldehyde and formyl chloride exhibit the largest enhancements.

In a polluted region such as the Los Angeles basin and outflow, Cl· will be primarily lost through reactions with VOC. Cl· reactivity as determined by the model is illustrated in Figure 4, where it is broken into Cl· reactions with methane, alkanes, alkenes, alcohols, carbonyls (aldehydes and ketones), and ozone. Other Cl· + VOC reactions, such as reactions with aromatics, are not shown as they were not a significant sink of Cl· relative to the species listed. In the morning (7 AM), the bulk of reactivity is due to reactions with a variety of alkanes, which comprise 42% of the 44 sec^{-1} total reactivity. Later in the day (3 PM), as the VOC are consumed in the model and O_3 maximizes, the reaction with O_3 to form ClO is the dominant Cl· sink and represents about 60% of the 39 sec^{-1} total reactivity. However, the majority of ClO (77% at 7 AM and 67% at 3 PM) will react with NO to give NO_2 and reform Cl· that can terminally react with VOC. Thus, we predict only 23 – 33% of the Cl· + O_3 reactions produce stable reservoirs like $ClONO_2$ and HOCl; though other studies predict even less for the Los Angeles region (Young et al., 2013). Over the course of the day, no single VOC dominates the Cl· reactivity (see Supplemental Figure S-119). Methane is consistently about 10% of the total. This implies that all VOC reactive towards Cl· are relevant when trying to estimate the total reactivity and that only using a small subset may significantly underestimate the total. This behavior is different from that of OH, the reactivity of which is often dominated by a few VOC or inorganic species such as CO and NO_2 in highly polluted regions (Kato et al., 2011; Ren et al., 2003).

3.2 Impact on RO_x and NO_x

The $ClNO_2$ formation described above leads to important and unique impacts on processes relevant to tropospheric air quality. Cl· produced by $ClNO_2$ photolysis will react with VOC to produce RO_2 during morning hours. The RO_2 will primarily react with NO under the polluted conditions to form HO_2 and closed-shell oxygenated VOC or an alkyl nitrate. Alternatively, given the large NO_2/NO ratio during the morning, enhanced peroxy nitrate formation is possible via reaction of acyl peroxy radicals with NO_2. The HO_2 produced via RO_2 + NO also reacts with NO to form OH, which in turn reacts with VOC to form RO_2. The chain length of this cycle tends to be somewhat short in the morning given higher concentrations of NO_x leading to termination via OH + NO_2 to form HNO_3 which is efficiently removed from the atmosphere through wet and dry deposition. Nonetheless, Cl· will enhance the abundance of

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morning time RO_x (OH + HO_2 + RO_2) as illustrated in Figure 5 which will lead to enhanced O_3 production rates relative to a model run without $ClNO_2$.

Figure 5A shows the HO_x production rate (P_{HOx}) for both the with- and without-$ClNO_2$ cases. A factor of 2.2 increase occurs in the early morning hours around 7 AM when Cl· production from $ClNO_2$ photolysis is the major Cl· source. P_{HOx} remains elevated throughout the day relative to the without-$ClNO_2$ case likely due to the larger ozone values in the with-$ClNO_2$ case, thus illustrating that the $ClNO_2$ influence persists for more than just the early morning hours. 24-hour integrated HO_x production for the with- and without-$ClNO_2$ cases is 75 ppbv and 62 ppbv, respectively. Uncertainties in modeling HONO have the largest impact on quantifying the perturbation of $ClNO_2$ to P_{HOx}. Constraining modeled HONO to the diel average values measured at the ground site results in the same overall pattern of $ClNO_2$ effects on P_{HOx} described above, just at a reduced relative magnitude – i.e., the inclusion of $ClNO_2$ formation increases P_{HOx} by ~35% in the morning, with moderate enhancements to P_{HOx} sustained throughout the day resulting in an integrated P_{HOx} of 116 ppbv and 105 ppbv for the with- and with-out $ClNO_2$ cases, respectively. These two extremes in terms of HONO are likely both representative – the latter HONO-rich case being representative of near surface chemistry while the former HONO-poor case is more representative of the residual boundary layer aloft of the surface, which dominatesnts the column-average radical budget as described by Young et al. (2012).

Figure 5B shows the effects of $ClNO_2$ on OH, HO_2, the sum over of all 717 organic peroxy radicals (RO_2), and the sum of all 140 acyl peroxy nitrates (APN) predicted by the model. The ratio of the with-$ClNO_2$ case relative to the without-$ClNO_2$ case is shown. Inclusion of $ClNO_2$ formation results in significant changes in HO_x (OH and HO_2) with 190% and 220% enhancements during the morning hours in OH and both HO_2 and RO_2, respectively. Such enhancements could be partly related to noted discrepancies between measured and modeled morning HO_x levels (Dusanter et al., 2009; Mao et al., 2010; Ren et al., 2003). Comparable enhancements in HO_2 and RO_2 were predicted by Osthoff et al. (2008) using the MCM to assess measurements taken in and around the Houston ship channel. In remote low-NO_x regions, Cl· and OH are largely uncoupled such that the presence of one does not largely impact the abundance of the other. This condition then allows indirect quantification of Cl· abundance by comparing VOC which have different reaction rate constants for reaction with OH and Cl· (i.e., Jobson et al. (1994), Platt et al. (2004), and Allan et al. (2007)). However, the presence of additional Cl· from $ClNO_2$ in a polluted region has the potential to significantly increase OH via the above mechanism, especially in the morning hours thereby muting this effect. Constraining modeled HONO again lowers the magnitude of these $ClNO_2$ induced morning perturbations to 25 and 50% increases in

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OH and the sum of HO_2 and RO_2, respectively. Again, while even these HONO-rich perturbations are significant, these findings, together with the vertically resolved estimates of Young et al. (2012), further imply that strong vertical gradients in HONO will influence the $ClNO_2$ effects on morning oxidant evolution.

$ClNO_2$ formation and photolysis has implications for the reactive nitrogen budget as well. $ClNO_2$ is relatively unreactive at night in these regions, thereby building up and allowing transport of NO_x downwind of the urban core with morning photolysis of $ClNO_2$ analogous to thermal decomposition of acyl peroxy nitrates such as PAN. In addition to this direct impact on NO_x transport, we find significant perturbations to acyl peroxy nitrate formation to occur in the with-$ClNO_2$ case (see Figure 5B). A 50% enhancement in total APN occurs before noon, and the enhancement remains elevated at around 10% for the remainder of the day. This $ClNO_2$ induced perturbation to APN formation largely persists even when measured HONO values are incorporated. Additionally, the sum of alkyl nitrates is also enhanced by 15% before noon with individual alkyl nitrates enhanced up to 60% in the with-$ClNO_2$ case. Increasing the partitioning of NO_x into reservoirs such as APN implies a greater potential for export of NO_x to remote regions. In fact, while $ClNO_2$ formation extends the lifetime of NO_x through the night, our model suggests that faster $OH + NO_2$, APN formation, and alkyl nitrate formation due to increased RO_x levels during the subsequent day largely offset this effect, such that NO_x is ~6% lower from sunrise until noon in the with-$ClNO_2$ than in the without-$ClNO_2$ case.

3.3 Impact on ozone production rate and odd-oxygen

We illustrate the influence of $ClNO_2$ chemistry on ozone production in Figure 5C (also see Supplemental Figure S-12). Over the entire model day, the difference between the integrated ozone production rate with 1.5 ppbv $ClNO_2$ and the integrated ozone production rate without $ClNO_2$ is about 12 ppbv. The majority of this enhancement takes place over the first 5 hours after sunrise where at 6:30 AM the ozone production rate is enhanced by ~200%. The pre-noon ozone mixing ratios relative to the without-$ClNO_2$ case are increased by ~20% with ~10% increase over the remainder of the day including peak ozone which occurs at about 5 PM. Such an influence is potentially large enough to affect attainment of air quality standards in polluted coastal regions where exceedences are often only tens of ppbv over the current standard (Parrish et al., 2010; Qin et al., 2004; U.S. EPA, 2006). The enhancement in ozone production scales nearly linearly with the $ClNO_2$ yield for this region, as expected, given that the ozone production rate is approximately linear with the primary radical source in a NO_x-saturated environment like Los Angeles. Constraining modeled HONO to the observations

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1 results in a slightly smaller 9 ppbv enhancement in the integrated ozone production rate due to ClNO$_2$

2 chemistry.

3

4 The above result is also interesting to consider in terms of the impact of nocturnal nitrogen oxide

5 chemistry on the odd-oxygen budget. Defining O$_x$ as the sum of O$_3$ and NO$_2$, our model predicts that

6 N$_2$O$_5$ reactions on aerosol particles consume 9 ppbv O$_x$ at night. If we neglect ClNO$_2$ formation, this 9

7 ppbv O$_x$ is permanently lost due to nitrate formation from N$_2$O$_5$ hydrolysis. However, incorporating

8 ClNO$_2$ formation, with a yield (branching ratio) of 50%, results in up to 12 ppbv O$_x$ produced the

9 subsequent day compared to the case where ClNO$_2$ formation is neglected. Thus, due to ClNO$_2$

10 formation and its daytime impact on oxidants and ozone, nighttime N$_2$O$_5$ chemistry does not net destroy

11 O$_x$ but is in fact potentially a net source, or at least a null cycle, for the Los Angeles region conditions

12 we simulate here.

13

14 While not directly comparable, our results appear generally consistent with a recent 3D CMAQ

15 modeling study of ClNO$_2$ effects on ozone and particulate nitrate (Sarwar et al., 2012). In the Los

16 Angeles region, the CMAQ modeling showed roughly a 2 – 4 ppbv increase in daytime ozone per ppbv

17 ClNO$_2$ photolyzed, with maxima approaching 8 ppbv/ppbv. Likely important in setting the actual ozone

18 enhancement caused by ClNO$_2$ is, among other possibilities, the extent to which a model mixes

19 background marine air with the polluted core during transport and the model predicted vertical

20 distribution of ClNO$_2$. These issues will be important to test with observations in order to validate

21 model representations of this process.

22

23 **4   Summary and conclusions**

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25 These model results suggest that ClNO$_2$ photolysis is likely a major Cl· source, if not the dominant

26 source, under conditions similar to those sampled in the Los Angeles region during CalNex 2010. The

27 impact of ClNO$_2$ on potential daytime halogen atom recycling is substantial, with significant enhancements

28 predicted on other Cl· reservoirs like ClONO$_2$, HOCl, and Cl$_2$. Relative to model runs without ClNO$_2$

29 formation, the presence of ClNO$_2$ causes significant and non-negligible perturbations in HO$_x$, RO$_2$, APN,

30 and ozone production. Relative to a model without ClNO$_2$ formation and heterogeneous HONO

31 production, incorporating ClNO$_2$ perturbed the integrated total radical and ozone production rates by

32 20%, with perturbations in RO$_x$ and APN >100%. Moreover, we show that, given these effects, the

33 impact of N$_2$O$_5$ reactions on aerosol particles is not a net sink of odd-oxygen but instead a net source for

34 the polluted coastal conditions we model here. The absolute magnitude of the perturbations in these

quantities and processes relative to a model that does not include $ClNO_2$ will ultimately depend upon the presence of HONO and the abundance of $ClNO_2$ and HONO vertically as well as seasonally.

We conclude by noting that during winter, in locations such as the Northeastern U.S., the role of $ClNO_2$ may be substantially more important to the total radical budget given that $O(^1D)$ production and H_2O vapor concentrations can both be factors of 5 lower than presented here, resulting in more than an order of magnitude reduction in primary OH abundances while $ClNO_2$ approaches similar concentrations (Kercher et al., 2009). This idea is consistent with the apparently important role of $ClNO_2$ at inland locations during wintertime as illustrated by recent studies at the Uintah Basin, Utah (Edwards et al., 2013).

1 **Figure Captions**

2

3 **Figure 1.** Model output for the analysis period of a model run showing $ClNO_2$ mixing ratios (heavy

4 green line, right y-axis) and Cl· concentrations for the case including $ClNO_2$ formation (heavy blue line,

5 left y-axis) and the case excluding $ClNO_2$ formation (dashed red line, left y-axis).

6

7 **Figure 2.** Model calculated Cl· production channels **(A)** without $ClNO_2$ formation (top) and **(B)** with

8 $ClNO_2$ formation (bottom).

9

10 **Figure 3.** Mixing ratios of various chlorinated species tracked in the model for the with-$ClNO_2$ model
11 case.

12

13 **Figure 4.** Modeled Cl· reactivity at 7 AM **(left)** and 3 PM **(right)** grouped by reactant types.

14

15 **Figure 5. (A)** The HO_x production rate with $ClNO_2$ formation (solid blue line) and without $ClNO_2$

16 formation (dashed red line). **(B)** The ratio of the hydroxyl radical (solid black line), hydroperoxyl

17 radical (dashed green line), sum of organic peroxy radicals (solid pink line), and sum of acyl peroxy

18 nitrates (dotted cyan line) for the with-$ClNO_2$ case relative to the without-$ClNO_2$ case. **(C)** The

19 difference between the integrated ozone production rate with $ClNO_2$ formation and the integrated ozone

20 production rate without $ClNO_2$ formation.

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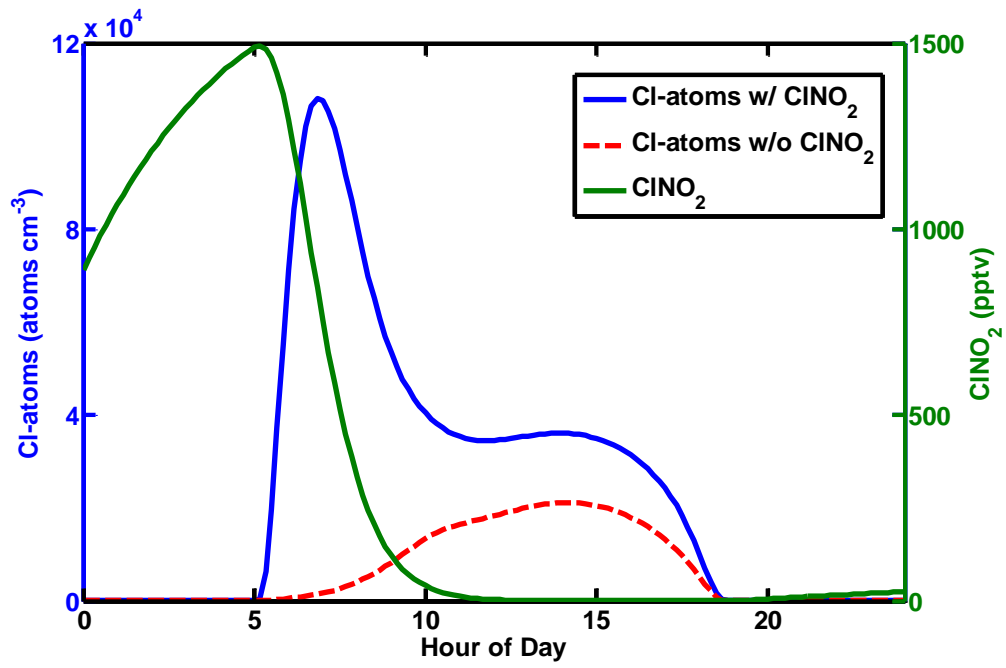
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1   FIGURES
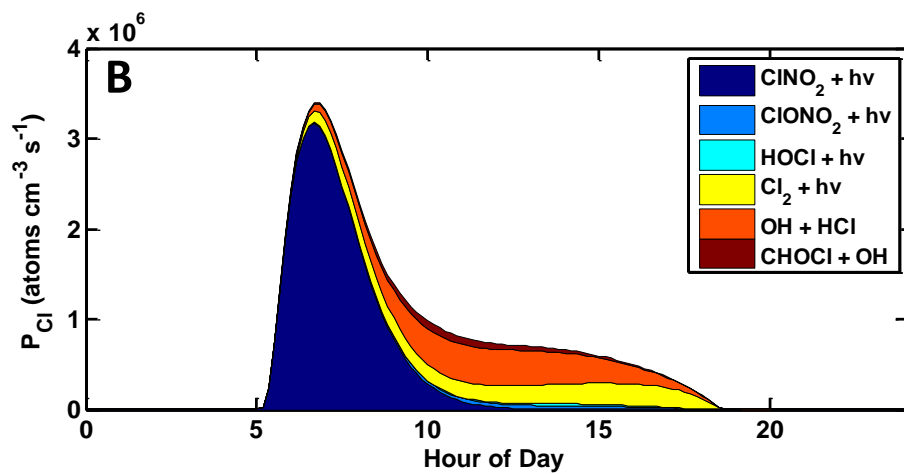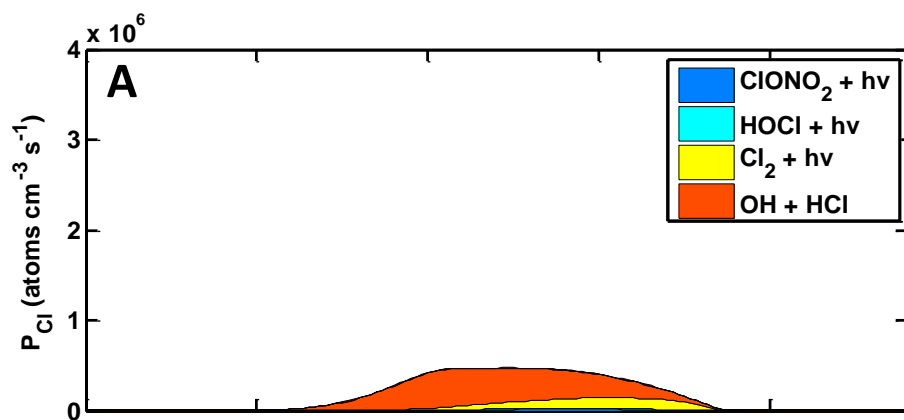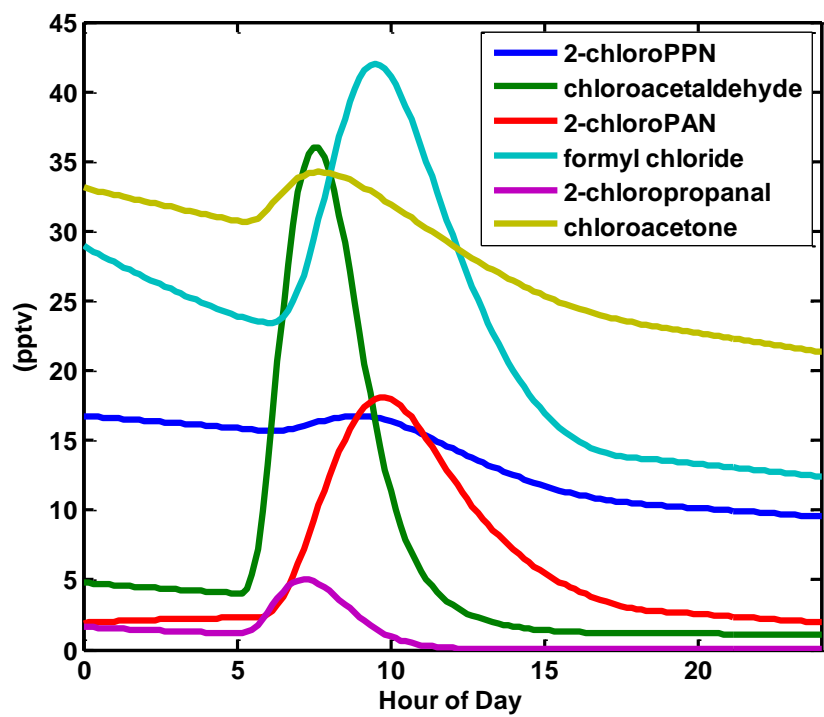

2

3   **Figure 1**
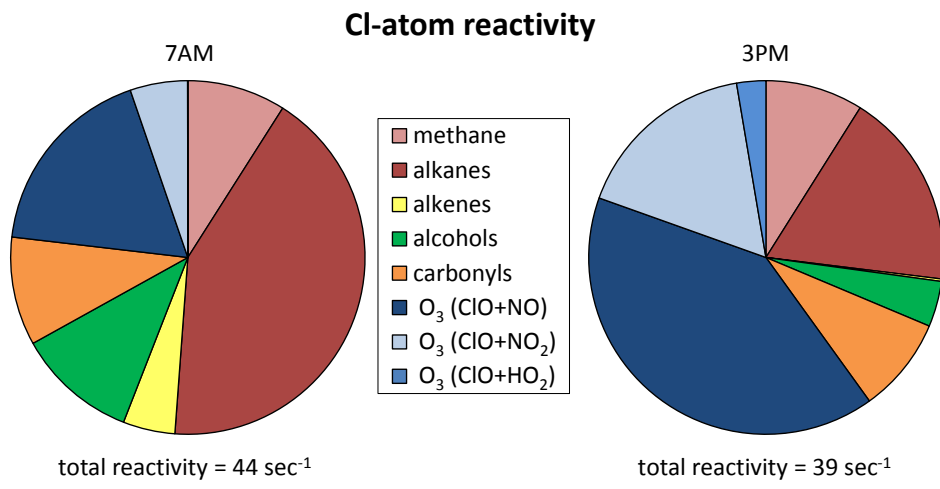
4

A

P_{Cl} (atoms cm^{-3} s^{-1})

x 10^6

- $ClONO_2$ + hv
- HOCl + hv
- Cl_2 + hv
- OH + HCl

B

P_{Cl} (atoms cm^{-3} s^{-1})

x 10^6

- $ClNO_2$ + hv
- $ClONO_2$ + hv
- HOCl + hv
- Cl_2 + hv
- OH + HCl
- CHOCl + OH

Hour of Day

Figure 2

1
2   **Figure 3**
3

Cl-atom reactivity

7AM

methane
alkanes
alkenes
alcohols
carbonyls
O_3 (ClO+NO)
O_3 (ClO+NO$_2$)
O_3 (ClO+HO$_2$)

total reactivity = 44 sec^{-1}

3PM

total reactivity = 39 sec^{-1}

1
2
3   **Figure 4**

35

Figure 5