

1 **An MCM modeling study of nitryl chloride (ClNO₂) impacts on**
2 **oxidation, ozone production and nitrogen oxide partitioning in polluted**
3 **continental outflow**

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1 **Abstract**

2
3 Nitryl chloride (ClNO₂) is produced at night by reactions of dinitrogen pentoxide (N₂O₅) on chloride
4 containing surfaces. ClNO₂ is photolyzed during the morning hours after sunrise to liberate highly
5 reactive chlorine atoms (Cl·). This chemistry takes place primarily in polluted environments where the
6 concentrations of N₂O₅ precursors (nitrogen oxide radicals and ozone) are high, though it likely occurs
7 in remote regions at lower intensities. Recent field measurements have illustrated the potential
8 importance of ClNO₂ as a daytime Cl· source and a nighttime NO_x reservoir. However, the fate of the
9 Cl· and the overall impact of ClNO₂ on regional photochemistry remain poorly constrained by
10 measurements and models. To this end, we have incorporated ClNO₂ production, photolysis, and
11 subsequent Cl· reactions into an existing Master Chemical Mechanism (MCM version 3.2) box model
12 framework using observational constraints from the CalNex 2010 field study. Cl· reactions with a set of
13 alkenes and alcohols, and the simplified multiphase chemistry of N₂O₅, ClNO₂, HOCl, ClONO₂, and
14 Cl₂, none of which are currently part of the MCM, have been added to the mechanism. The presence of
15 ClNO₂ produces significant changes to oxidants, ozone, and nitrogen oxide partitioning, relative to
16 model runs excluding ClNO₂ formation. From a nighttime maximum of 1.5 ppbv ClNO₂, the daytime
17 maximum Cl· concentration reaches 1x10⁵ atoms cm⁻³ at 7 AM, reacting mostly with a large suite of
18 volatile organic compounds (VOC) to produce 2.2 times more organic peroxy radicals in the morning
19 than in the absence of ClNO₂. In the presence of several ppbv of nitrogen oxide radicals (NO_x = NO +
20 NO₂), these perturbations lead to similar enhancements in hydrogen oxide radicals (HO_x = OH + HO₂).
21 Neglecting contributions from HONO, the total integrated daytime radical source is 17% larger when
22 including ClNO₂, which leads to a similar enhancement in integrated ozone production of 15%.
23 Detectable levels (tens of pptv) of chlorine containing organic compounds are predicted to form as a
24 result of Cl· addition to alkenes, which may be useful in identifying times of active Cl· chemistry.

26 **1 Introduction**

27
28 Chlorine atoms (Cl·) are highly reactive, often having rate constants for reactions with volatile organic
29 compounds (VOC) that are factors of 10 to 200 larger than the hydroxyl radical, OH, which is
30 considered the atmosphere's primary initiator of oxidation. As a result, the presence of Cl· can lead to
31 shorter lifetimes for VOC and an enhanced radical pool which can potentially enhance the production of
32 ozone in polluted areas. The global tropospheric Cl· budget remains uncertain, with a large range in
33 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.



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 HNO₃ and H₂SO₄ (Keene et al., 2007). Cl· formed by HCl + OH tend to peak around
14 midday with the peak in OH formed from O(¹D) + H₂O. 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 (Cl₂) 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). Cl₂ mixing ratios
20 were often on the order of tens of pptv with maximum reported mixing ratios near 100 – 200 pptv.
21 Direct Cl₂ emissions are related to power generation, water treatment, and oil refineries (Sarwar and
22 Bhave, 2007). Recently, a low pH Cl₂ production channel that may be atmospherically relevant has been
23 identified in the reaction of N₂O₅ with chloride containing substrates, which involved ClONO₂ as an
24 intermediate (Roberts et al., 2008). In addition, Cl₂ can be formed in situ through multiphase chemistry
25 involving chlorine nitrate (ClONO₂) 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 Cl₂. In polluted
27 air, the reaction of ClO with NO, which completes a null cycle producing Cl· and NO₂, limits the
28 potential for multiphase Cl₂ formation.

29

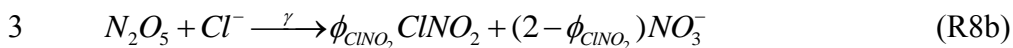
30 BrCl photolysis to form Cl· and atomic bromine is also thought to be an important Cl· source, especially
31 in remote regions. In polar regions, BrCl mixing ratios on the order of tens of pptv have been measured
32 (Buys et al., 2013; Foster et al., 2001; Spicer et al., 2002). To our knowledge there have been no
33 reported observations of BrCl in ambient air outside of polar regions (Finley and Saltzman, 2008). BrCl

1 can form through heterogeneous reactions of BrONO₂ and HOBr on acidic, chloride-containing
2 particles in an analogous manner to the Cl₂ formation reactions described above or through reactions of
3 ClONO₂ and HOCl on acidic, bromide-containing particles.

4
5 Nitrosyl chloride (ClNO) has also been proposed as a potential Cl· source (Raff et al., 2009). These
6 theoretical and laboratory studies have yet to be confirmed by field measurements of ClNO in ambient
7 air. Using a regional 3-D chemical transport model, Raff et al. predict that ClNO mixing ratios in
8 polluted marine areas could reach ppbv values. That said, the hydrolysis of ClNO at moderate and high
9 relative humidity (RH>20%) will likely be sufficiently rapid to prevent the buildup of appreciable
10 atmospheric concentrations of ClNO (Karlsson and Ljungström, 1996; Rubasinghege and Grassian,
11 2012; Scheer et al., 1997).

12
13 Since its proposed atmospheric formation by Finlayson-Pitts et al. (1989) and first observation in
14 ambient air by Osthoff et al. (2008), nitryl chloride (ClNO₂) has been observed during a number of
15 different field studies worldwide with nighttime maximum mixing ratios ranging from tens of pptv to
16 over 2 ppbv (Kercher et al., 2009; Mielke et al., 2011; Mielke et al., 2013; Osthoff et al., 2008; Phillips
17 et al., 2012; Riedel et al., 2012a; Thornton et al., 2010; Young et al., 2012). These observations have
18 occurred in both continental and marine locations illustrating the importance of ClNO₂ as a Cl· source in
19 a variety of different environments. ClNO₂ represents a Cl· source with clear anthropogenic origins as it
20 is formed at night by reactions involving NO_x (NO₂ + NO), ozone, and chloride containing aerosols.
21 Anthropogenic activities associated with power generation, motor vehicle use, and agriculture now
22 dominate the global NO_x source (Jaegle et al., 2005). Natural sources of NO_x, such as microbial activity,
23 lightning, and wildfires, are also significant globally, but the impact of these NO_x sources on ClNO₂
24 formation remain unknown. At night, a fraction of NO_x is converted into ClNO₂ through Reactions R6 –
25 R8. The branching ratio between Reactions R8a and R8b, commonly referred to as the ClNO₂ yield (
26 ϕ_{ClNO_2}), is determined by the efficiency of ClNO₂ formation from heterogeneous reactions of N₂O₅. The
27 ϕ_{ClNO_2} and the N₂O₅-particle reaction probability, $\gamma(N_2O_5)$, are uncertain quantities that can vary
28 significantly depending on a number of factors such as particulate water, chloride, nitrate, and organic
29 content (Badger et al., 2006; Bertram and Thornton, 2009; McNeill et al., 2006; Mentel et al., 1999;
30 Thornton et al., 2003). After sunrise, the photolysis of ClNO₂ produces Cl· and NO₂, thereby partially
31 circumventing the removal of NO_x through the formation and loss of 2HNO₃ (R8a).

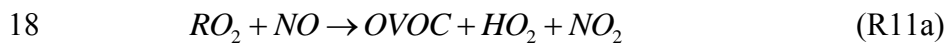
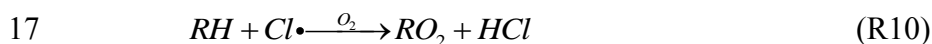
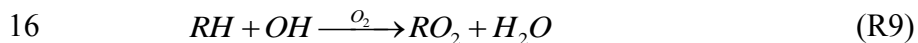




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5 The Cl· budget, hydrogen oxide and organic peroxy radical abundance ($RO_x = OH + HO_2 + RO_2$), NO_x
6 lifetime and partitioning among other forms of reactive nitrogen, and the net ozone production rate are
7 linked through photochemical oxidation 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



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

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 ClNO₂ 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 ClNO₂ 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 ClNO₂ 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 (May 16 – 31) due to the added constraints provided by the Pasadena ground site
24 measurements. ClNO₂ 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,

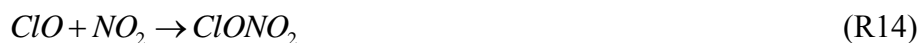
1 such as reactions of alkoxy radicals, are treated as instantaneous in order to reduce model stiffness.

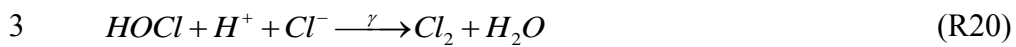
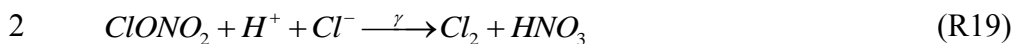
2
3 In total, 44 of the VOC measured at the Pasadena site are used to constrain the model. However, certain
4 VOC, for example, ethanol (median value = 8.2 ppbv) and acetone (median value = 3.8 ppbv), measured
5 at the Pasadena ground site appeared to often be dominated by highly localized emissions. To more
6 generally represent an urban air mass in the model, ground site VOC measurements were scaled by
7 those measured on the R/V *Atlantis*. A smaller number of VOC were measured aboard the R/V *Atlantis*,
8 so species not represented in the R/V *Atlantis* dataset were scaled by species of similar structure (i.e.,
9 similar functional groups). For example, methanol was measured with median levels of approximately 6
10 ppbv and 1 ppbv at the ground site and on the ship, respectively. Ethanol, however, was only measured
11 at the ground site. To estimate ethanol levels in the urban outflow and be more representative of what
12 the R/V *Atlantis* might have sampled, the ground site ethanol mixing ratios were simply scaled down by
13 1/6. For a complete list of the measured VOC used in the model see Supplemental Information Table S-
14 1.

15
16 VOC and HCl mixing ratios are held to their ship-scaled hourly average diurnal profiles for a 69 hour
17 “spin-up” period. The diurnal HCl profile used is shown in Supplemental Figure S-1. NO₂, O₃, and CO
18 are held to mean values measured at the ground site during this spin-up period. In addition, we fix
19 methane at a mixing ratio of 1.8 ppmv. Over the entirety of a model run temperature is held constant at
20 25 °C and the aerosol surface area concentration is held constant at 350 μm² cm⁻³, which represents
21 some of the largest aerosol surface area concentrations encountered by the R/V *Atlantis* while sampling
22 Los Angeles outflow. At lower model temperatures a larger fraction of NO_x will react as N₂O₅ with
23 higher ClNO₂ levels and an increased morning Cl· burden relative to warmer cases. This result suggests
24 that we are possibly overestimating the actual yield of ClNO₂ per NO₂ oxidized by ozone at night. The
25 box model does not attempt to replicate the effects of meteorology and thus the processes of dilution
26 and deposition are not accurately incorporated. To maintain reasonable concentrations of the many
27 modeled species which were not constrained by observations, we apply a continuous dilution rate of
28 1.5% per hour to all species. Formaldehyde and nitric acid have an additional deposition rate of 30% per
29 hour in order to keep mixing ratios at levels most similar to those sampled during the CalNex study (<6
30 ppbv for formaldehyde) (Warneke et al., 2011). The sensitivity of the results to this additional loss rate
31 is minor (<20% adjustments to the Cl· budget), and the need for this additional loss is likely related to
32 our neglect of deposition for intermediate organic oxidation products (in the case of formaldehyde) and
33 of HNO₃ itself. Isoprene, alpha-pinene, beta-pinene, and limonene are allowed to freely evolve at night
34 during the spin-up period to avoid unrealistic conditions whereby NO₃ reactions with these compounds

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

7
8 A number of reactions necessary for evaluating Cl· production and reactivity are not included in the
9 MCM. Version 3.2 of the MCM only includes Cl· reactions with alkanes. In order to accurately
10 represent the chemistry, multiple mechanisms were added to the model framework. These include the
11 Reactions R1 – R3, R8, R13 – R21, and a number of VOC + Cl· reactions such as those for methanol,
12 ethanol, isopropanol, ethene, propene, formaldehyde, ethanal, propanal, acetone, benzene, styrene, o-
13 xylene, toluene. Several of the added mechanisms are explicitly shown in the Supplemental Information
14 (Supplemental Figure S-2 – S-6). A complete list of the added reactions and reaction rate constants is
15 given in Supplemental Table S-2, and the MATLAB code is freely available for download at
16 <ftp://ftp.atmos.washington.edu/thornton/UWCM/>. The reaction rate constants and product branching for
17 these reactions were taken from the IUPAC kinetics database as of May 11, 2012. Chlorinated products
18 not present in the MCM or available in the IUPAC database were assumed to react similarly and with
19 similar rate constants to non-chlorinated species of the same structure already in the MCM (see
20 Supplemental Table S-2). Additionally, our revised mechanism explicitly tracks gas-phase HCl
21 formation that results from hydrogen atom abstraction reactions by Cl·. ClONO₂ photolysis frequencies
22 were estimated by scaling measured NO₂ photolysis frequencies down by a factor of 30 (i.e., $j_{NO_2}/30$).
23 This approximation produces ClONO₂ photolysis frequencies close to observations taken aboard the R/V
24 *Atlantis* (Supplemental Figure S-7). Photolysis frequencies for Cl₂, ClONO₂, and HOCl were calculated
25 using the Tropospheric Ultraviolet and Visible (TUV) Radiation Model (available at
26 <http://cprm.acd.ucar.edu/Models/TUV>) and incorporated into the box model.





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 \cdot chemistry in future studies. As we show below, such compounds
9 could be another avenue for Cl \cdot recycling. Reactions of Cl \cdot 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 \cdot 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 \cdot +
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 \cdot reactivity, it would be necessary to include a more
15 explicit isoprene oxidation mechanism to accurately capture the effects Cl \cdot , 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 $_2$ O $_5$, 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 ClONO $_2$ formation, we vary ϕ_{ClONO_2} between 0% and 50% in successive model
32 runs, which produce a without-ClONO $_2$ case and a with-ClONO $_2$ case, respectively. A 50% yield results in
33 ~1.5 ppbv of ClONO $_2$ as shown in Figure 1, which is similar to levels in the Los Angeles outflow

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 ClNO₂
5 and HONO throughout the nocturnal and evolving daytime boundary layer are likely different (Young et
6 al., 2012), making our primary focus on ClNO₂ a reasonable simplification for a box model.

8 **3 Results and discussion**

10 *3.1 Cl-atom budget*

12 The model predicts that, integrated over a typical day in the Los Angeles outflow, ClNO₂ is the major
13 driver of Cl· evolution. Neither HCl + OH nor multiphase chemistry involving ClONO₂ and HOCl to
14 produce Cl₂ are competitive with the ClNO₂ 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-ClNO₂ and
17 without-ClNO₂ cases. When ClNO₂ formation is included, the Cl· concentration reaches a maximum at
18 ~7 AM (2 hours after model sunrise) with a value of 1.08x10⁵ atoms cm⁻³. A substantially different
19 picture results from the without-ClNO₂ case where the maximum Cl· concentration occurs around noon
20 and only reaches 0.2x10⁵ atoms cm⁻³. The assumptions made about the aerosol reaction probabilities of
21 ClONO₂ 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 ClONO₂ 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 ClONO₂ and HOCl reaction probability and a 100% Cl₂ yield is likely more realistic as the formation of
28 Cl₂ 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 ClONO₂
30 especially needs to be better constrained.

32 The evolution of Cl· largely follows that of the dominant source terms, as shown in Figure 2. In the
33 absence of ClNO₂ formation (Fig. 2A), the bulk of Cl· production results from the HCl + OH production
34 channel, and the maximum in Cl· production rate of 0.5x10⁶ atoms cm⁻³ s⁻¹ coincides with the maximum

1 production from the HCl + OH channel. In the with-ClONO₂ case (Fig. 2B), the maximum Cl· production
2 rate occurs at 7 AM with a value of 3.4×10^6 atoms cm⁻³ s⁻¹ corresponding to the maximum contribution
3 from ClONO₂ photolysis. The ClONO₂ production channel represents 56% of Cl· production over the
4 course of the entire day, leading to nearly 3.7 times as many Cl· produced relative to the without-ClONO₂
5 case. By noon, ClONO₂ is largely depleted under the clear-sky model conditions, and other Cl· production
6 channels like the reaction of HCl with OH and the photolysis of Cl₂ from HOCl and ClONO₂
7 heterogeneous chemistry become more dominant. These production channels involving multi-phase Cl-
8 recycling to form Cl₂ show significant enhancements when ClONO₂ formation is included. For example,
9 Cl· production from ClONO₂ photolysis, HOCl photolysis, and Cl₂ photolysis are enhanced by factors
10 of 3.3, 2.2, and 3.3, respectively over the without-ClONO₂ case. To some extent these enhancements
11 should be expected considering the larger Cl· pool available for recycling reactions when ClONO₂
12 formation is allowed, but they give indication of the degree of indirect coupling between ClONO₂ and Cl₂
13 via the increased formation of reactive chlorine reservoirs like ClONO₂ and HOCl. During CalNex,
14 molecular chlorine was also measured along with ClONO₂ (Riedel et al., 2012a). Observations of
15 nighttime and early morning Cl₂ were typically in the 5 – 50 pptv range. Modeled Cl₂ levels are of
16 similar magnitude to these observations, as well as previous observations of Cl₂ in this region (Finley
17 and Saltzman, 2006, 2008), and show a morning enhancement with slightly elevated levels throughout
18 the day but only with the inclusion of ClONO₂ (see Supplemental Figure S-8). For additional information
19 on the model concentrations of the Cl· source species see Supplemental Figure S-9.

20

21 Given the lack of BrCl observations outside of polar regions, we do not include BrCl formation in the
22 model and therefore do not explicitly account for the potential Cl· source, if any, represented by BrCl.
23 Considering Cl₂ represents 16% of the integrated Cl· source over the course of a model day, the typical
24 seawater ratio of chloride to bromide of ~650:1, and assuming that BrCl formation is not significantly
25 faster than 650 times Cl₂ formation, we estimate an upper limit Cl· source from BrCl resulting from
26 ClONO₂ and HOCl reactions that is similar to that predicted from Cl₂. That said, BrCl formed from
27 these reactions should not significantly bias our Cl· estimates considering that we force these reactants
28 to produce exclusively Cl₂, the photolysis of which forms 2Cl· compared to only 1Cl· from BrCl
29 photolysis. However, heterogeneous reactions of BrONO₂ and HOBr to form BrCl are not accounted for
30 at all. Using maximum HCl levels as a measure of particulate chloride displaced over Los Angeles and
31 the expected chloride to bromide ratio in seawater, 2.5 ppbv of chloride corresponds to ~4 pptv of
32 bromide available for BrCl formation. Incorporating this amount of total bromine into the model and
33 assuming $\gamma(\text{BrONO}_2)$ and $\gamma(\text{HOBr}) = 0.1$ with a unit yield of BrCl, we predict the model could be
34 neglecting a Cl· source from BrCl on the order of 5% of the Cl· concentration integrated over the model

1 day. Ambient measurements of BrCl in polluted coastal regions would be a particularly useful constraint
2 on the extent of these Cl[·] recycling reactions and the role of bromide.

3
4 The use of a comprehensive chemical mechanism such as the MCM also illustrates a potentially
5 important but heretofore overlooked source of Cl[·] in polluted regions. In the with-ClONO₂ case, the
6 reaction of OH with formyl chloride (CHOCl), produced from Cl[·] attack of alkenes, becomes a
7 noticeable Cl[·] source during the afternoon. Interestingly, CHOCl photolysis is predicted to be a Cl[·]
8 source comparable in magnitude to that from HOCl photolysis (Figure 2B). In fact, because we possibly
9 overestimate the actual multi-phase recycling of ClONO₂ and HOCl to form Cl₂, Cl[·] release from such
10 acid chlorides may be more important than these multiphase processes in regions with significant alkene
11 concentrations. This result suggests observations of acid chlorides would be as beneficial as Cl₂ in
12 polluted regions.

13
14 HONO has a noticeable impact on the afternoon Cl[·] budget via photolysis to form OH followed by the
15 reaction of OH + HCl. Constraining the model to the HONO diurnal profile measured at the Pasadena
16 ground site leads to a 60% increase (1.4×10^7 to 2.26×10^7 molecules cm⁻³) in the daily maximum OH
17 concentration and a similar increase in the integrated Cl[·] formation rate from OH + HCl. Multiphase
18 recycling via ClONO₂ and HOCl are also increased as a result of the larger Cl[·] concentrations.
19 However, as discussed by Young et al. (2012), afternoon and daytime HONO concentrations are fairly
20 uncertain, especially when considering the extent to which HONO measurements over land represent
21 HONO concentrations in the marine boundary layer during morning hours within an air mass that was
22 transported offshore overnight.

23
24 We also investigate the formation potential of chlorinated products at potentially detectable quantities
25 resulting from the Cl[·] oxidation of VOC. These species could represent “tracers” of Cl[·] chemistry and
26 indicate the extent to which Cl[·] oxidation reactions are occurring. This issue has been investigated
27 previously in the Houston area using ground based measurements of potential products from Cl[·]
28 oxidation of isoprene (Riemer et al., 2008). As stated above, chlorinated products of Cl[·] reactions with
29 isoprene are not included our model and are likely of minor importance to total Cl[·] reactivity in the Los
30 Angeles region. Within our model framework, Cl[·] addition reactions with ethene and propene can
31 produce chlorinated products such as 2-chloroperoxypropionyl nitrate (2-chloroPPN),
32 chloroacetaldehyde, 2-chloroperoxyacetyl nitrate (2-chloroPAN), formyl chloride, 2-chloropropanal,
33 and chloroacetone – some of which have been previously investigated in polar regions (Keil and
34 Shepson, 2006). As with most of the previously mentioned effects, these enhancements are pronounced

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

4
5 In a polluted region such as the Los Angeles basin and outflow, Cl[·] will be primarily lost through
6 reactions with VOC. Cl[·] reactivity as determined by the model is illustrated in Figure 4, where it is
7 broken into Cl[·] reactions with methane, alkanes, alkenes, alcohols, carbonyls (aldehydes and ketones),
8 and ozone. Other Cl[·] + VOC reactions, such as reactions with aromatics, are not shown as they were not
9 a significant sink of Cl[·] relative to the species listed. In the morning (7 AM), the bulk of reactivity is due
10 to reactions with a variety of alkanes, which comprise 42% of the 44 sec⁻¹ total reactivity. Later in the
11 day (3 PM), as the VOC are consumed in the model and O₃ maximizes, the reaction with O₃ to form
12 ClO is the dominant Cl[·] sink and represents about 60% of the 39 sec⁻¹ total reactivity. However, the
13 majority of ClO (77% at 7 AM and 67% at 3 PM) will react with NO to give NO₂ and reform Cl[·] that
14 can terminally react with VOC. Thus, we predict only 23 – 33% of the Cl[·] + O₃ reactions produce stable
15 reservoirs like ClONO₂ and HOCl; though other studies predict even less for the Los Angeles region
16 (Young et al., 2013). Over the course of the day, no single VOC dominates the Cl[·] reactivity (see
17 Supplemental Figure S-11). Methane is consistently about 10% of the total. This implies that all VOC
18 reactive towards Cl[·] are relevant when trying to estimate the total reactivity and that only using a small
19 subset may significantly underestimate the total. This behavior is different from that of OH, the
20 reactivity of which is often dominated by a few VOC or inorganic species such as CO and NO₂ in
21 highly polluted regions (Kato et al., 2011; Ren et al., 2003).

22 23 3.2 Impact on RO_x and NO_x

24
25 The ClONO₂ formation described above leads to important and unique impacts on processes relevant to
26 tropospheric air quality. Cl[·] produced by ClONO₂ photolysis will react with VOC to produce RO₂ during
27 morning hours. The RO₂ will primarily react with NO under the polluted conditions to form HO₂ and
28 closed-shell oxygenated VOC or an alkyl nitrate. Alternatively, given the large NO₂/NO ratio during the
29 morning, enhanced peroxy nitrate formation is possible via reaction of acyl peroxy radicals with NO₂.
30 The HO₂ produced via RO₂ + NO also reacts with NO to form OH, which in turn reacts with VOC to
31 form RO₂. The chain length of this cycle tends to be somewhat short in the morning given higher
32 concentrations of NO_x leading to termination via OH + NO₂ to form HNO₃ which is efficiently removed
33 from the atmosphere through wet and dry deposition. Nonetheless, Cl[·] will enhance the abundance of

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

3
4 Figure 5A shows the HO_x production rate (P_{HO_x}) for both the with- and without- $ClNO_2$ cases. A factor
5 of 2.2 increase occurs in the early morning hours around 7 AM when $Cl\cdot$ production from $ClNO_2$
6 photolysis is the major $Cl\cdot$ source. P_{HO_x} remains elevated throughout the day relative to the without-
7 $ClNO_2$ case likely due to the larger ozone values in the with- $ClNO_2$ case, thus illustrating that the
8 $ClNO_2$ influence persists for more than just the early morning hours. 24-hour integrated HO_x production
9 for the with- and without- $ClNO_2$ cases is 75 ppbv and 62 ppbv, respectively. Uncertainties in modeling
10 HONO have the largest impact on quantifying the perturbation of $ClNO_2$ to P_{HO_x} . Constraining modeled
11 HONO to the diel average values measured at the ground site results in the same overall pattern of
12 $ClNO_2$ effects on P_{HO_x} described above, just at a reduced relative magnitude – i.e., the inclusion of
13 $ClNO_2$ formation increases P_{HO_x} by ~35% in the morning, with moderate enhancements to P_{HO_x}
14 sustained throughout the day resulting in an integrated P_{HO_x} of 116 ppbv and 105 ppbv for the with- and
15 with-out $ClNO_2$ cases, respectively. These two extremes in terms of HONO are likely both
16 representative – the latter HONO-rich case being representative of near surface chemistry while the
17 former HONO-poor case is more representative of the residual boundary layer aloft of the surface,
18 which dominates the column-average radical budget as described by Young et al. (2012).

19
20 Figure 5B shows the effects of $ClNO_2$ on OH , HO_2 , the sum of all 717 organic peroxy radicals (RO_2),
21 and the sum of all 140 acyl peroxy nitrates (APN) predicted by the model. The ratio of the with- $ClNO_2$
22 case relative to the without- $ClNO_2$ case is shown. Inclusion of $ClNO_2$ formation results in significant
23 changes in HO_x (OH and HO_2) with 190% and 220% enhancements during the morning hours in OH
24 and both HO_2 and RO_2 , respectively. Such enhancements could be partly related to noted discrepancies
25 between measured and modeled morning HO_x levels (Dusanter et al., 2009; Mao et al., 2010; Ren et al.,
26 2003). Comparable enhancements in HO_2 and RO_2 were predicted by Osthoff et al. (2008) using the
27 MCM to assess measurements taken in and around the Houston ship channel. In remote low- NO_x
28 regions, $Cl\cdot$ and OH are largely uncoupled such that the presence of one does not largely impact the
29 abundance of the other. This condition then allows indirect quantification of $Cl\cdot$ abundance by
30 comparing VOC which have different reaction rate constants for reaction with OH and $Cl\cdot$ (i.e., Jobson
31 et al. (1994), Platt et al. (2004), and Allan et al. (2007)). However, the presence of additional $Cl\cdot$ from
32 $ClNO_2$ in a polluted region has the potential to significantly increase OH via the above mechanism,
33 especially in the morning hours thereby muting this effect. Constraining modeled HONO again lowers
34 the magnitude of these $ClNO_2$ induced morning perturbations to 25 and 50% increases in OH and the

1 sum of HO₂ and RO₂, respectively. Again, while even these HONO-rich perturbations are significant,
2 these findings, together with the vertically resolved estimates of Young et al. (2012), further imply that
3 strong vertical gradients in HONO will influence the ClNO₂ effects on morning oxidant evolution.

4
5 ClNO₂ formation and photolysis has implications for the reactive nitrogen budget as well. ClNO₂ is
6 relatively unreactive at night in these regions, thereby building up and allowing transport of NO_x
7 downwind of the urban core with morning photolysis of ClNO₂ analogous to thermal decomposition of
8 acyl peroxy nitrates such as PAN. In addition to this direct impact on NO_x transport, we find significant
9 perturbations to acyl peroxy nitrate formation to occur in the with-ClNO₂ case (see Figure 5B). A 50%
10 enhancement in total APN occurs before noon, and the enhancement remains elevated at around 10%
11 for the remainder of the day. This ClNO₂ induced perturbation to APN formation largely persists even
12 when measured HONO values are incorporated. Additionally, the sum of alkyl nitrates is also enhanced
13 by 15% before noon with individual alkyl nitrates enhanced up to 60% in the with-ClNO₂ case.
14 Increasing the partitioning of NO_x into reservoirs such as APN implies a greater potential for export of
15 NO_x to remote regions. In fact, while ClNO₂ formation extends the lifetime of NO_x through the night,
16 our model suggests that faster OH + NO₂, APN formation, and alkyl nitrate formation due to increased
17 RO_x levels during the subsequent day largely offset this effect, such that NO_x is ~6% lower from sunrise
18 until noon in the with-ClNO₂ than in the without-ClNO₂ case.

20 *3.3 Impact on ozone production rate and odd-oxygen*

21
22 We illustrate the influence of ClNO₂ chemistry on ozone production in Figure 5C (also see
23 Supplemental Figure S-12). Over the entire model day, the difference between the integrated ozone
24 production rate with 1.5 ppbv ClNO₂ and the integrated ozone production rate without ClNO₂ is about
25 12 ppbv. The majority of this enhancement takes place over the first 5 hours after sunrise where at 6:30
26 AM the ozone production rate is enhanced by ~200%. The pre-noon ozone mixing ratios relative to the
27 without-ClNO₂ case are increased by ~20% with ~10% increase over the remainder of the day including
28 peak ozone which occurs at about 5 PM. Such an influence is potentially large enough to affect
29 attainment of air quality standards in polluted coastal regions where exceedences are often only tens of
30 ppbv over the current standard (Parrish et al., 2010; Qin et al., 2004; U.S. EPA, 2006). The
31 enhancement in ozone production scales nearly linearly with the ClNO₂ yield for this region, as
32 expected, given that the ozone production rate is approximately linear with the primary radical source in
33 a NO_x-saturated environment like Los Angeles. Constraining modeled HONO to the observations

1 results in a slightly smaller 9 ppbv enhancement in the integrated ozone production rate due to ClNO₂
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 O₃ and NO₂, our model predicts that
6 N₂O₅ reactions on aerosol particles consume 9 ppbv O_x at night. If we neglect ClNO₂ formation, this 9
7 ppbv O_x is permanently lost due to nitrate formation from N₂O₅ hydrolysis. However, incorporating
8 ClNO₂ 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 ClNO₂ formation is neglected. Thus, due to ClNO₂
10 formation and its daytime impact on oxidants and ozone, nighttime N₂O₅ 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 ClNO₂ 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 ClNO₂ photolyzed, with maxima approaching 8 ppbv/ppbv. Likely important in setting the actual ozone
18 enhancement caused by ClNO₂ 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 ClNO₂. 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**

24
25 These model results suggest that ClNO₂ 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 ClNO₂ on potential daytime halogen atom recycling is substantial, with significant enhancements
28 predicted on other Cl· reservoirs like ClONO₂, HOCl, and Cl₂. Relative to model runs without ClNO₂
29 formation, the presence of ClNO₂ causes significant and non-negligible perturbations in HO_x, RO₂, APN,
30 and ozone production. Relative to a model without ClNO₂ formation and heterogeneous HONO
31 production, incorporating ClNO₂ 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 N₂O₅ 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

1 quantities and processes relative to a model that does not include ClNO₂ will ultimately depend upon the
2 presence of HONO and the abundance of ClNO₂ and HONO vertically as well as seasonally.

3
4 We conclude by noting that during winter, in locations such as the Northeastern U.S., the role of ClNO₂
5 may be substantially more important to the total radical budget given that O(¹D) production and H₂O
6 vapor concentrations can both be factors of 5 lower than presented here, resulting in more than an order
7 of magnitude reduction in primary OH abundances while ClNO₂ approaches similar concentrations
8 (Kercher et al., 2009). This idea is consistent with the apparently important role of ClNO₂ at inland
9 locations during wintertime as illustrated by recent studies at the Uintah Basin, Utah (Edwards et al.,
10 2013).

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20 study.

1 **Figure Captions**

2

3 **Figure 1.** Model output for the analysis period of a model run showing ClNO₂ mixing ratios (heavy
4 green line, right y-axis) and Cl· concentrations for the case including ClNO₂ formation (heavy blue line,
5 left y-axis) and the case excluding ClNO₂ formation (dashed red line, left y-axis).

6

7 **Figure 2.** Model calculated Cl· production channels **(A)** without ClNO₂ formation (top) and **(B)** with
8 ClNO₂ formation (bottom).

9

10 **Figure 3.** Mixing ratios of various chlorinated species tracked in the model for the with-ClNO₂ 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 ClNO₂ formation (solid blue line) and without ClNO₂
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-ClNO₂ case relative to the without-ClNO₂ case. **(C)** The
19 difference between the integrated ozone production rate with ClNO₂ formation and the integrated ozone
20 production rate without ClNO₂ formation.

21

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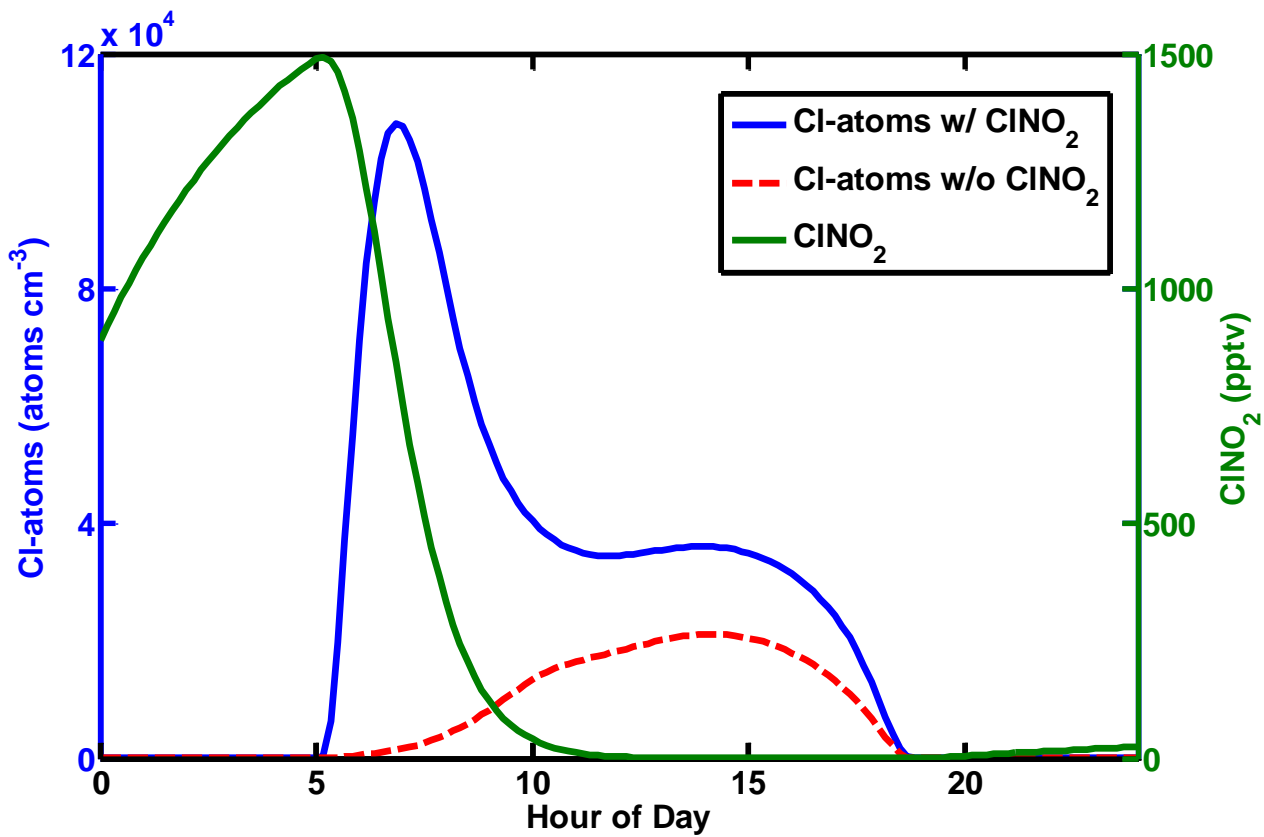
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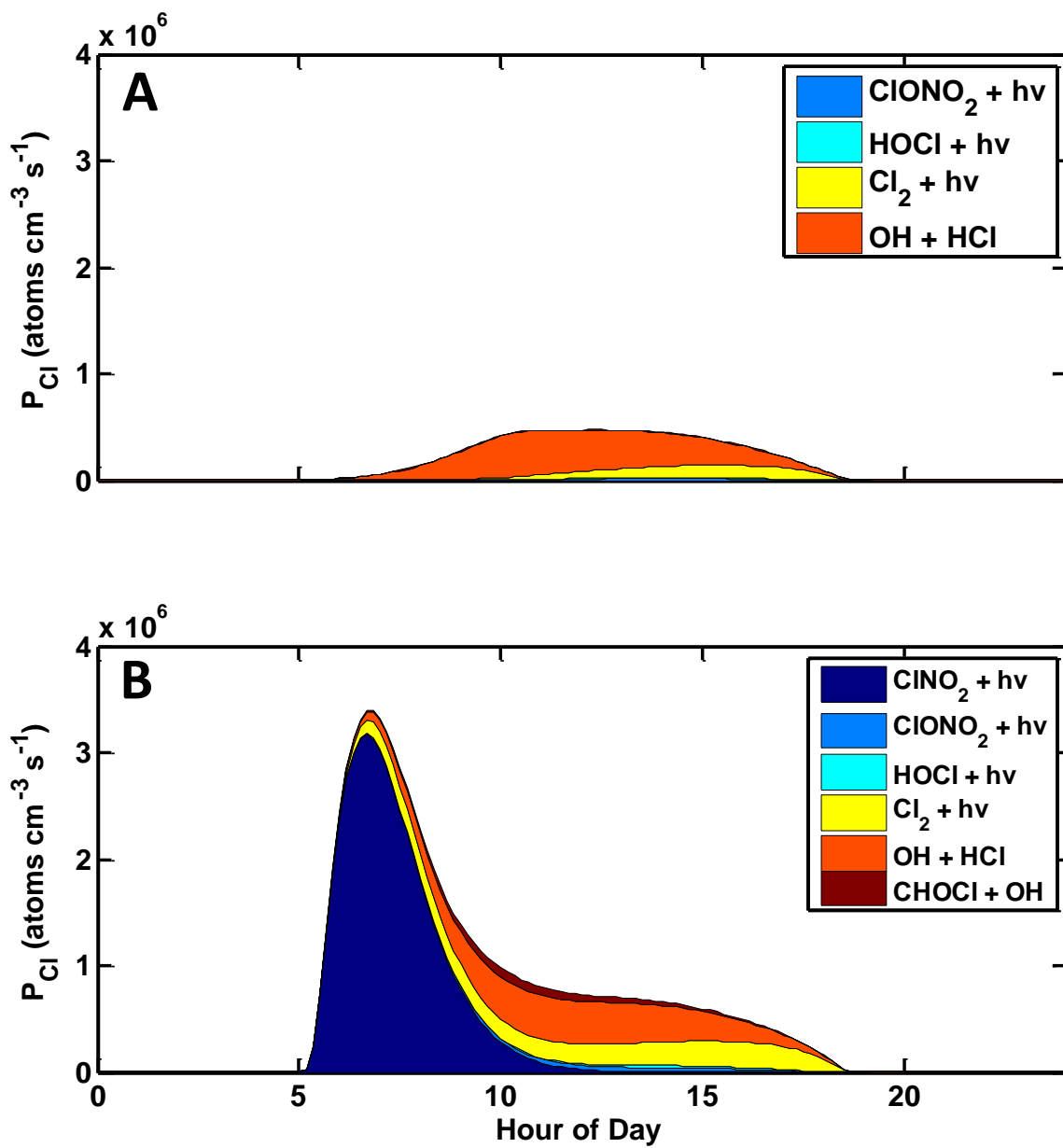
1 FIGURES



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3 Figure 1

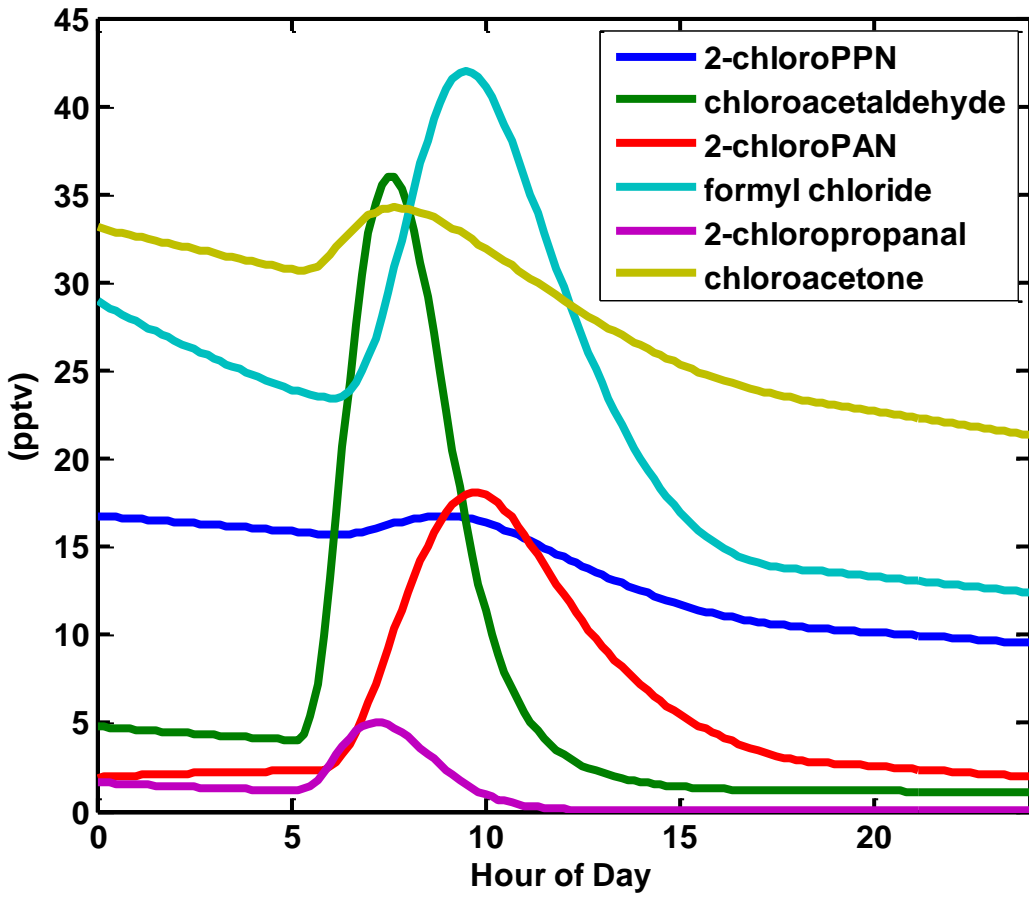
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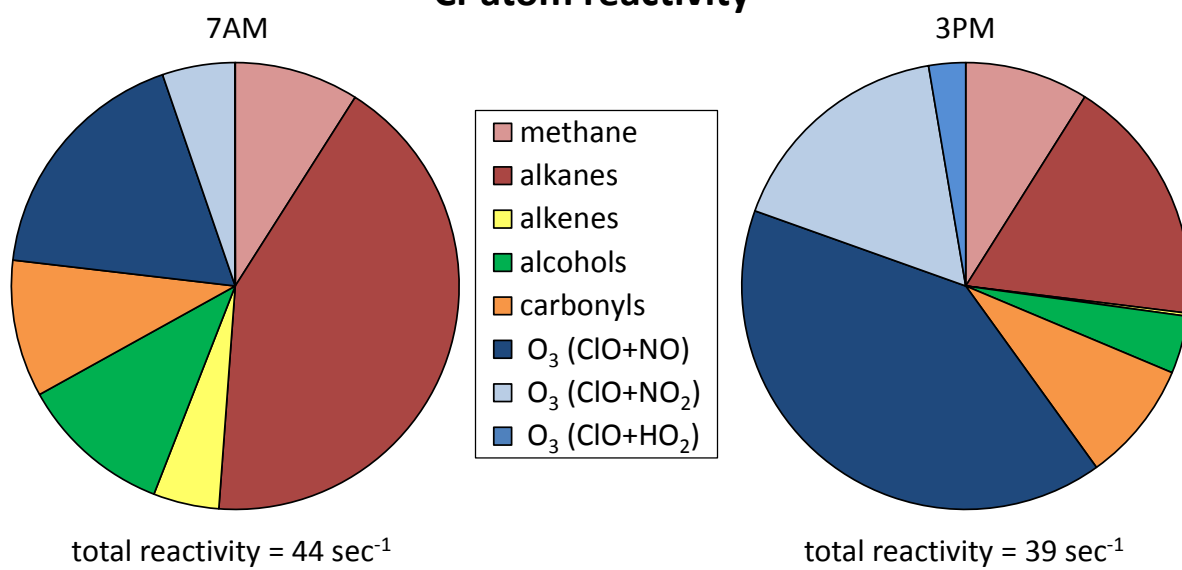
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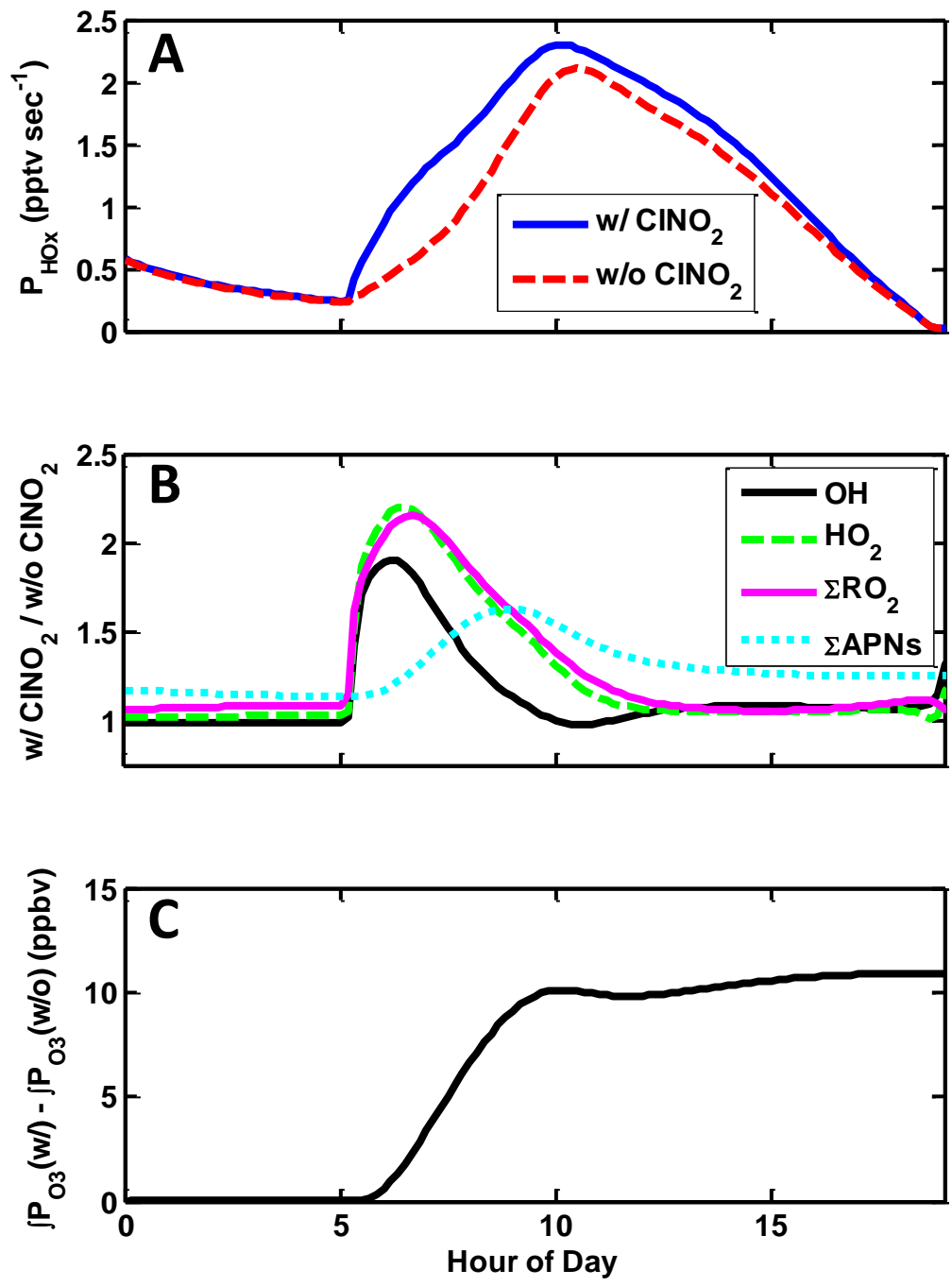
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Figure 3

Cl-atom reactivity



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Figure 4



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