



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

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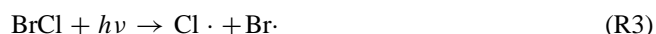
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Abstract. Nitryl chloride (ClNO₂) is produced at night by reactions of dinitrogen pentoxide (N₂O₅) on chloride containing surfaces. ClNO₂ is photolyzed during the morning hours after sunrise to liberate highly reactive chlorine atoms (Cl·). This chemistry takes place primarily in polluted environments where the concentrations of N₂O₅ 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 ClNO₂ as a daytime Cl· source and a nighttime NO_x reservoir. However, the fate of the Cl· and the overall impact of ClNO₂ on regional photochemistry remain poorly constrained by measurements and models. To this end, we have incorporated ClNO₂ 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 N₂O₅, ClNO₂, HOCl, ClONO₂, and Cl₂, none of which are currently part of the MCM, have been added to

the mechanism. The presence of ClNO₂ produces significant changes to oxidants, ozone, and nitrogen oxide partitioning, relative to model runs excluding ClNO₂ formation. From a nighttime maximum of 1.5 ppbv ClNO₂, the daytime maximum Cl· concentration reaches 1×10^5 atoms cm⁻³ at 07:00 model time, 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 ClNO₂. In the presence of several ppbv of nitrogen oxide radicals (NO_x = NO + NO₂), these perturbations lead to similar enhancements in hydrogen oxide radicals (HO_x = OH + HO₂). Neglecting contributions from HONO, the total integrated daytime radical source is 17 % larger when including ClNO₂, 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) as tropospheric Cl· concentrations are not presently measurable by existing methods. There are a number of potential Cl· sources in the troposphere, the major sources are outlined in Reactions (R1)–(R5).



The reaction of hydrochloric acid (HCl) with the hydroxyl radical (OH) is a daytime source of Cl·. Typical HCl mixing ratios in the troposphere vary from 100–5000 pptv with the highest found in polluted regions with direct HCl emissions from industrial processes and acid displacement of aqueous chloride by HNO₃ and H₂SO₄ (Keene et al., 2007). Cl· formed by HCl + OH tend to peak around midday with the peak in OH formed from O(¹D) + H₂O. Additionally, the oxidation of many VOC by Cl· proceeds via a hydrogen abstraction to form HCl, thus recycling this Cl· source.

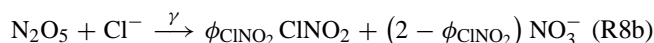
Photolysis of molecular chlorine (Cl₂) produces two Cl· and has been the focus of many Cl· investigations since it was first measured at elevated concentrations in ambient air (Finley and Saltzman, 2006, 2008; Lawler et al., 2011; Riedel et al., 2012a; Spicer et al., 1998). Cl₂ mixing ratios were often on the order of tens of pptv with maximum reported mixing ratios near 100–200 pptv. Direct Cl₂ emissions are related to power generation, water treatment, and oil refineries (Sarwar and Bhave, 2007). Recently, a low pH Cl₂ production channel that may be atmospherically relevant has been identified in the reaction of N₂O₅ with chloride containing substrates, which involved ClNO₂ as an intermediate (Roberts et al., 2008). In addition, Cl₂ can be formed in situ through multiphase chemistry involving chlorine nitrate (ClONO₂) and hypochlorous acid (HOCl). These species, in turn, can photolyze to reform Cl· or ClO or react on acidic, chloride-containing particles to form Cl₂. In polluted air, the reaction of ClO with NO, which completes a null cycle producing Cl· and NO₂, limits the potential for multiphase Cl₂ formation.

BrCl photolysis to form Cl· and atomic bromine is also thought to be an important Cl· source, especially in remote regions. In polar regions, BrCl mixing ratios on the order of tens of pptv have been measured (Buys et al., 2013; Foster et al., 2001; Spicer et al., 2002). To our knowledge there have been no reported observations of BrCl in ambient air outside of polar regions (Finley and Saltzman, 2008). BrCl can form through heterogeneous reactions of BrONO₂ and HOBr on acidic, chloride-containing particles in an analogous manner to the Cl₂ formation reactions described above or through reactions of ClONO₂ and HOCl on acidic, bromide-containing particles.

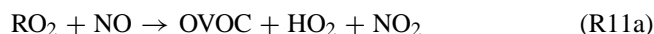
Nitrosyl chloride (ClNO) has also been proposed as a potential Cl· source (Raff et al., 2009). These theoretical and laboratory studies have yet to be confirmed by field measurements of ClNO in ambient air. Using a regional 3-D chemical transport model, Raff et al. (2009) predict that ClNO mixing ratios 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 (ClNO₂) 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, 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 ClNO₂ as a Cl· source in a variety of different environments. ClNO₂ represents a Cl· source with clear anthropogenic origins as it is formed at night by reactions involving NO_x (NO₂ + 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 ClNO₂ formation remain unknown. At night, a fraction of NO_x is converted into ClNO₂ through Reactions (R6)–(R8). The branching ratio between Reactions R8a and R8b, commonly referred to as the ClNO₂ yield (ϕ_{ClNO_2}), is determined by the efficiency of ClNO₂ formation from heterogeneous reactions of N₂O₅. The ϕ_{ClNO_2} and the N₂O₅-particle reaction probability, γ (N₂O₅), 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 ClNO₂ produces Cl· and NO₂, thereby partially circumventing the removal of NO_x through

the formation and loss of 2 HNO₃ (Reaction R8a).



The Cl· budget, hydrogen oxide and organic peroxy radical abundance (RO_x = OH + HO₂ + RO₂), NO_x lifetime and partitioning among other forms of reactive nitrogen, and the net ozone production rate are linked through photochemical oxidation of VOC. As shown in Reactions (R9)–(R12), the oxidation of a hydrocarbon (RH) is initiated by reaction with OH or Cl· to form the organic peroxy radical (RO₂). In polluted regions, the dominant fate of RO₂ is to react with NO. The dominant channel of this reaction eventually leads to a closed shell oxygenated hydrocarbon (OVOC – oxygenated volatile organic compound), hydroperoxyl radical (HO₂) and NO₂, while the minor channel leads to an alkyl nitrate (RONO₂). If the RO₂ is an acyl peroxy radical, then reaction with NO₂ produces acyl peroxy nitrates (APN) such as acetyl peroxy nitrate (PAN). NO also reacts with HO₂ to form NO₂ and OH. Through these reactions ozone is produced from the photolysis of NO₂.



From the above discussion, we expect that ClNO₂ acts similarly, though not exactly the same, as an OH source such as that from nitrous acid (HONO) photolysis or O(¹D) + H₂O. When the radical pool is terminated via cross reactions between RO_x and NO_x, a higher production rate of HO_x or Cl· will nearly linearly increase the ozone production rate (Daum et al., 2000; Kleinman, 2005). Moreover, at high NO, production of an RO₂ by Cl· attack directly increases the steady state concentration of OH and HO₂ due to the rapid cycling between OH, HO₂ and RO₂. However, the increased RO₂ due to Cl· arises from a potentially different pool of hydrocarbons than that from OH, given the large differences in RH abundance and relative reactivity towards OH and Cl·. Moreover, ClNO₂ photolysis predominantly occurs in the first few hours after sunrise, well before the maximum OH production rate from O(¹D) + H₂O and before the maximum in NO/NO₂. Thus, the full impact of ClNO₂ on ozone production, VOC lifetime and NO_x abundance and partitioning may not be the same as simply scaling the daytime average HO_x production rate.

Here we examine the effects of ClNO₂ formation as predicted by a detailed box model that incorporates the master chemical mechanism and is constrained by ground and ship-based ambient measurements taken during the CalNex 2010 field study. The aim is not to replicate specific observations or conditions, but rather to use the model to develop conceptual insights into the effect of a morning pulse of chlorine atoms in polluted air. We use the model to assess the impact of ClNO₂ on the Cl· budget, RO_x abundance, NO_x lifetime and partitioning, and the net ozone production rate.

2 Measurements and model description

We chose to constrain a box model using data taken during the CalNex field study, which occurred in May and June of 2010 in the southern California region (Ryerson et al., 2013). 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 NO_x in polluted coastal regions. There were multiple measurement platforms involved in CalNex, three of which recorded both ClNO₂ and extensive VOC measurements: the Research Vessel *Atlantis*, a ground site located on the California Institute of Technology campus in Pasadena, CA, and aircraft measurements taken on the NOAA WP-3D (Mielke et al., 2013; Riedel et al., 2012a; Young et al., 2012). Though the R/V *Atlantis* sampled in many locations along the southern California coast, we focus on the measurements made in and around Los Angeles urban outflow (16–31 May) due to the added constraints provided by the Pasadena ground site measurements. ClNO₂ mixing ratios in the nocturnal outflow from the Los Angeles region were commonly over 500 pptv with maximums on the order of 2 ppbv (Riedel et al., 2012a; Wagner et al., 2012).

Cl· chemistry was incorporated into an existing model framework described in Wolfe and Thornton (2011) which is based on the master chemical mechanism version 3.2 (MCM) developed at the University of Leeds (more information available at <http://mcm.leeds.ac.uk/MCM>) (Bloss et al., 2005; Jenkin et al., 1997, 2003; Saunders et al., 2003). Use of the MCM allows for explicit tracking of approximately 2800 chemical species and about 9000 different reactions with reaction rate constants derived from the International Union of Pure and Applied Chemistry (IUPAC) kinetics database (<http://www.iupac-kinetic.ch.cam.ac.uk>). Similar to Wolfe and Thornton (2011), fast reactions, such as reactions of alkoxy radicals, are treated as instantaneous in order to reduce model stiffness.

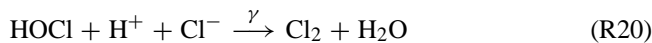
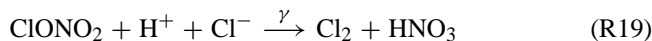
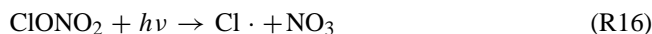
In total, 44 of the VOC measured at the Pasadena site are used to constrain the model. However, certain VOC, for example, ethanol (median value = 8.2 ppbv) and acetone (median value = 3.8 ppbv), measured at the Pasadena ground site appeared to often be dominated by highly localized

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* data set were scaled by species of similar structure (i.e., similar functional groups). For example, methanol was measured with median levels of approximately 6 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 one-sixth. For a complete list of the measured VOC used in the model see Table S1 in the Supplement.

VOC and HCl mixing ratios are held to their ship-scaled hourly average diurnal profiles for a 69 h “spin-up” period. The diurnal HCl profile used is shown in Fig. S1 in the Supplement. NO₂, O₃, 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 μm² 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 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. 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 HNO₃ 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 NO₃ reactions with these compounds 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 h.

We use the final 24 h 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 (Figs. S2–S6 in the Supplement). A complete list of the added reactions and reaction rate constants is given in Table S2 in the Supplement, 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 11 May 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 Table S2 in the Supplement). Additionally, our revised mechanism explicitly tracks gas-phase HCl formation that results from hydrogen atom abstraction reactions by Cl·. ClNO₂ photolysis frequencies were estimated by scaling measured NO₂ photolysis frequencies down by a factor of 30 (i.e., $j_{\text{NO}_2}/30$). This approximation produces ClNO₂ photolysis frequencies close to observations taken aboard the R/V *Atlantis* (Fig. S7 in the Supplement). Photolysis frequencies for Cl₂, ClONO₂, 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.



For alkenes, the major pathway involves addition of chlorine to the double bond rather than the typical hydrogen abstraction pathway (Atkinson et al., 2004). This pathway leads

to chlorinated products which might be detectable as tracers of Cl· chemistry in future studies. As we show below, such compounds could be another avenue for Cl· recycling. Reactions of Cl· with isoprene, which also produces unique chlorinated products, were not included in the model framework given its modest < 1 % contribution to total Cl· reactivity in the modeled Los Angeles outflow and the large increase in complexity when incorporating the mechanism (Fan and Zhang, 2004; Tanaka et al., 2003). Instead, the products of Cl· + isoprene were tracked as a single generic species with no chemical losses. However, in areas where isoprene is a more significant contributor to Cl· reactivity, it would be necessary to include a more explicit isoprene oxidation mechanism to accurately capture the effects of Cl·, especially to assess any chlorinated products that might form from these reactions (Riemer et al., 2008). In such locations the products of chlorine-initiated isoprene oxidation are likely more pronounced than in the Los Angeles region.

Gas-particle reaction probabilities in the model are set to 0.01 for N₂O₅, ClONO₂, and HOCl (Reactions R8, R19, R20). A $\gamma = 0.01$ is within the typical range of γ (N₂O₅) measured on ambient aerosol (< 0.001–0.03) at elevated RH during various field studies (Bertram et al., 2009; Riedel et al., 2012b). Laboratory measurements of ClONO₂ and HOCl uptake under stratospheric and tropospheric conditions on sulfuric acid, sodium chloride, and sodium bromide particles and pure water droplets generally report γ values < 0.06 for ClONO₂ and HOCl (Deiber et al., 2004; Hanson and Ravishankara, 1994; Hanson et al., 1994). We make the upper-limit assumption that reactions of ClONO₂ and HOCl on aerosol particles produce only Cl₂ with unit efficiency. Given that Cl₂ production from heterogeneous reactions of ClONO₂ and HOCl is proportional to the product of γ and the yield, we use $\gamma = 0.01$ and a 100 % yield on all particles in the model.

To examine the effects of ClNO₂ formation, we vary ϕ_{ClNO_2} between 0 and 50 % in successive model runs, which produce a without-ClNO₂ case and a with-ClNO₂ case, respectively. A 50 % yield results in ~ 1.5 ppbv of ClNO₂ as shown in Fig. 1, which is similar to levels in the Los Angeles outflow conditions encountered during CalNex. We also performed a series of model runs where HONO was constrained to observations made at the Pasadena ground site. Its abundance otherwise is determined only by the reaction of OH + NO, HONO + OH, and the photolysis of HONO. Most of our main conclusions reported here are relatively insensitive to HONO. Moreover, the vertical profiles of ClNO₂ and HONO throughout the nocturnal and evolving daytime boundary layer are likely different (Young et al., 2012), making our primary focus on ClNO₂ a reasonable simplification for a box model.

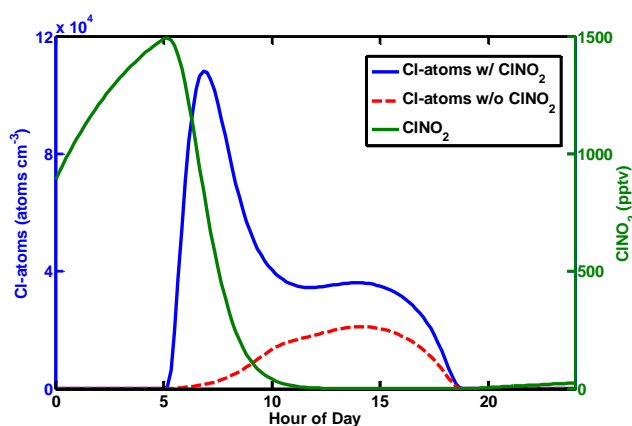


Fig. 1. Model output for the analysis period of a model run showing ClNO₂ mixing ratios (heavy green line, right y axis) and Cl· concentrations for the case including ClNO₂ formation (heavy blue line, left y axis) and the case excluding ClNO₂ formation (dashed red line, left y axis).

3 Results and discussion

3.1 Cl-atom budget

The model predicts that, integrated over a typical day in the Los Angeles outflow, ClNO₂ is the major driver of Cl· evolution. Neither HCl + OH nor multiphase chemistry involving ClONO₂ and HOCl to produce Cl₂ are competitive with the ClNO₂ source. Moreover, this picture is consistent with that derived solely from observations in this region (Riedel et al., 2012a). Figure 1 shows the Cl· concentration predicted by the model during the 24 h analysis period for both the with-ClNO₂ and without-ClNO₂ cases. When ClNO₂ formation is included, the Cl· concentration reaches a maximum at $\sim 07:00$ model time (2 h after model sunrise) with a value of 1.08×10^5 atoms cm⁻³. A substantially different picture results from the without-ClNO₂ case where the maximum Cl· concentration occurs around noon and only reaches 0.2×10^5 atoms cm⁻³. The assumptions made about the aerosol reaction probabilities of ClONO₂ and HOCl partially drive the late afternoon Cl· profile, which, as a result, is more uncertain. However, this afternoon Cl· concentration profile is not especially sensitive to the assumed reaction probabilities. For example, increasing the reaction probabilities of ClONO₂ and HOCl from 0.01 to 0.1 does not substantially change the 24 h profile. The maximum in Cl· concentration is increased by ~ 10 % still occurring in the early morning hours after sunrise ($\sim 07:00$ model time), and the integrated Cl· concentration over the entire day is enhanced by only 20 %. Additionally, the choice of 0.01 for a ClONO₂ and HOCl reaction probability and a 100 % Cl₂ yield is likely more realistic as the formation of Cl₂ from these reactions is unlikely to be the sole product (Caloz et al., 1996; Santschi and Rossi, 2005). That said, to fully understand the impact

of Cl· chemistry in coastal urban areas, the fate of ClONO₂ especially needs to be better constrained.

The evolution of Cl· largely follows that of the dominant source terms, as shown in Fig. 2. In the absence of ClONO₂ formation (Fig. 2a), the bulk of Cl· production results from the HCl + OH production channel, and the maximum in Cl· production rate of 0.5×10^6 atoms cm⁻³ s⁻¹ coincides with the maximum production from the HCl + OH channel. In the with-ClONO₂ case (Fig. 2b), the maximum Cl· production rate occurs at 07:00 model time with a value of 3.4×10^6 atoms cm⁻³ s⁻¹ corresponding to the maximum contribution from ClONO₂ photolysis. The ClONO₂ 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-ClONO₂ case. By noon, ClONO₂ is largely depleted under the clear-sky model conditions, and other Cl· production channels such as the reaction of HCl with OH and the photolysis of Cl₂ from HOCl and ClONO₂ heterogeneous chemistry become more dominant. These production channels involving multi-phase Cl-recycling to form Cl₂ show significant enhancements when ClONO₂ formation is included. For example, Cl· production from ClONO₂ photolysis, HOCl photolysis, and Cl₂ photolysis are enhanced by factors of 3.3, 2.2, and 3.3, respectively, over the without-ClONO₂ case. To some extent these enhancements should be expected considering the larger Cl· pool available for recycling reactions when ClONO₂ formation is allowed, but they give indication of the degree of indirect coupling between ClONO₂ and Cl₂ via the increased formation of reactive chlorine reservoirs like ClONO₂ and HOCl. During CalNex, molecular chlorine was also measured along with ClONO₂ (Riedel et al., 2012a). Observations of nighttime and early morning Cl₂ were typically in the 5–50 pptv range. Modeled Cl₂ levels are of similar magnitude to these observations, as well as previous observations of Cl₂ 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 ClONO₂ (see Fig. S8 in the Supplement). For additional information on the model concentrations of the Cl· source species see Fig. S9 in the Supplement.

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 Cl₂ 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 Cl₂ formation, we estimate an upper limit Cl· source from BrCl resulting from ClONO₂ and HOCl reactions that is similar to that predicted from Cl₂. That said, BrCl formed from these reactions should not significantly bias our Cl· estimates considering that we force these reactants to produce exclusively Cl₂, the photolysis of which forms 2 Cl· compared to only 1 Cl· from BrCl photolysis. However, heterogeneous reactions of BrONO₂ and

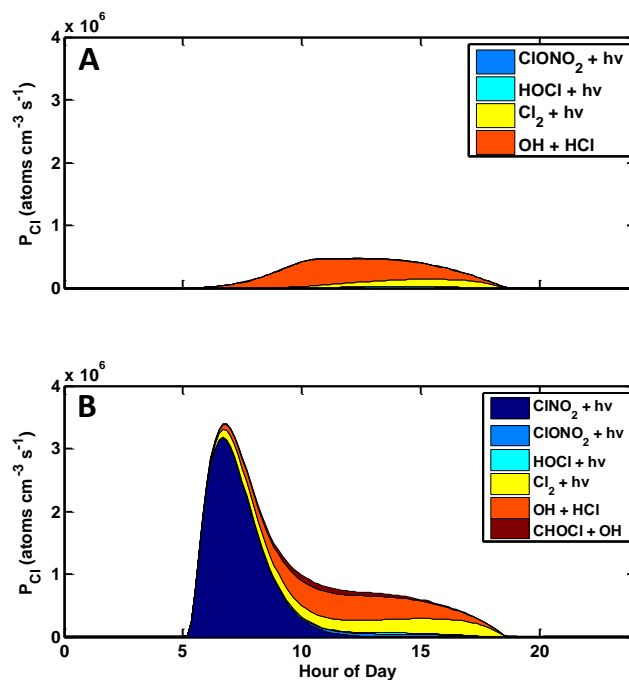


Fig. 2. Model calculated Cl· production channels (A) without ClONO₂ formation and (B) with ClONO₂ formation.

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 $\gamma(\text{BrONO}_2)$ and $\gamma(\text{HOBr}) = 0.1$ 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 day. Ambient measurements of BrCl in polluted coastal regions would be a particularly useful constraint on the extent of these Cl· 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· in polluted regions. In the with-ClONO₂ case, the reaction of OH with formyl chloride (CHOCl), produced from Cl· attack of alkenes, becomes a noticeable Cl· source during the afternoon. Interestingly, CHOCl photolysis is predicted to be a Cl· source comparable in magnitude to that from HOCl photolysis (Fig. 2b). In fact, because we possibly overestimate the actual multi-phase recycling of ClONO₂ and HOCl to form Cl₂, Cl· release from such acid chlorides may be more important than these multi-phase processes in regions with significant alkene concentrations. This result suggests observations of acid chlorides would be as beneficial as Cl₂ in polluted regions.

HONO has a noticeable impact on the afternoon Cl· budget via photolysis to form OH followed by the reaction

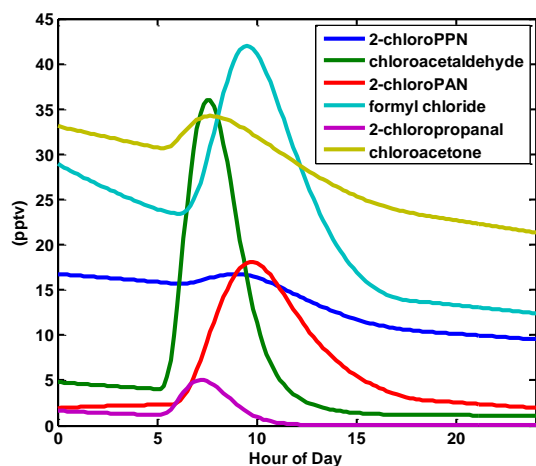


Fig. 3. Mixing ratios of various chlorinated species tracked in the model for the with-ClNO₂ model case.

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· formation rate from OH + HCl. Multiphase recycling via ClONO₂ and HOCl are also increased as a result of the larger Cl· 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· oxidation of VOC. These species could represent “tracers” of Cl· chemistry and indicate the extent to which Cl· oxidation reactions are occurring. This issue has been investigated previously in the Houston area using ground-based measurements of potential products from Cl· oxidation of isoprene (Riemer et al., 2008). As stated above, chlorinated products of Cl· reactions with isoprene are not included our model and are likely of minor importance to total Cl· reactivity in the Los Angeles region. Within our model framework, Cl· 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 in the early part of the day when Cl· and VOC concentrations are highest in the model. As we show in Fig. 3, morning enhancements are typically on the

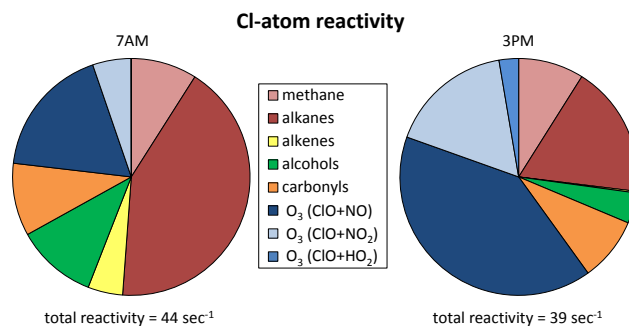


Fig. 4. Modeled Cl· reactivity at 07:00 model time (left panel) and 15:00 model time (right panel) grouped by reactant types.

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 Fig. 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 (07:00 model time), the bulk of reactivity is due to reactions with a variety of alkanes, which comprise 42 % of the 44 s^{-1} total reactivity. Later in the day (15:00 model time), as the VOC are consumed in the model and O₃ maximizes, the reaction with O₃ 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 07:00 model time and 67 % at 15:00 model time) will react with NO to give NO₂ and reform Cl· that can terminally react with VOC. Thus, we predict only 23–33 % of the Cl· + O₃ reactions produce stable reservoirs like ClONO₂ 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 Fig. S11 in the Supplement). 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 NO₂ in highly polluted regions (Kato et al., 2011; Ren et al., 2003).

3.2 Impact on RO_x and NO_x

The ClNO₂ formation described above leads to important and unique impacts on processes relevant to tropospheric air quality. Cl· produced by ClNO₂ photolysis will react with VOC to produce RO₂ during morning hours. The RO₂ will

primarily react with NO under the polluted conditions to form HO₂ and closed-shell oxygenated VOC or an alkyl nitrate. Alternatively, given the large NO₂/NO ratio during the morning, enhanced peroxy nitrate formation is possible via reaction of acyl peroxy radicals with NO₂. The HO₂ produced via RO₂ + NO also reacts with NO to form OH, which in turn reacts with VOC to form RO₂. 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 + NO₂ to form HNO₃ which is efficiently removed from the atmosphere through wet and dry deposition. Nonetheless, Cl· will enhance the abundance of morning time RO_x (OH + HO₂ + RO₂) as illustrated in Fig. 5 which will lead to enhanced O₃ production rates relative to a model run without CINO₂.

Figure 5a shows the HO_x production rate (P_{HO_x}) for both the with- and without-CINO₂ cases. A factor of 2.2 increase occurs in the early morning hours around 07:00 model time when Cl· production from CINO₂ photolysis is the major Cl· source. P_{HO_x} remains elevated throughout the day relative to the without-CINO₂ case likely due to the larger ozone values in the with-CINO₂ case, thus illustrating that the CINO₂ influence persists for more than just the early morning hours. 24 h integrated HO_x production for the with- and without-CINO₂ cases is 75 and 62 ppbv, respectively. Uncertainties in modeling HONO have the largest impact on quantifying the perturbation of CINO₂ to P_{HO_x} . Constraining modeled HONO to the diel average values measured at the ground site results in the same overall pattern of CINO₂ effects on P_{HO_x} described above, just at a reduced relative magnitude – that is, the inclusion of CINO₂ formation increases P_{HO_x} by ~35 % in the morning, with moderate enhancements to P_{HO_x} sustained throughout the day resulting in an integrated P_{HO_x} of 116 and 105 ppbv for the with- and without-CINO₂ 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 dominates the column-average radical budget as described by Young et al. (2012).

Figure 5b shows the effects of CINO₂ on OH, HO₂, the sum of all 717 organic peroxy radicals (RO₂), and the sum of all 140 acyl peroxy nitrates (APN) predicted by the model. The ratio of the with-CINO₂ case relative to the without-CINO₂ case is shown. Inclusion of CINO₂ formation results in significant changes in HO_x (OH and HO₂) with 190 and 220 % enhancements during the morning hours in OH and both HO₂ and RO₂, 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 HO₂ and RO₂ 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

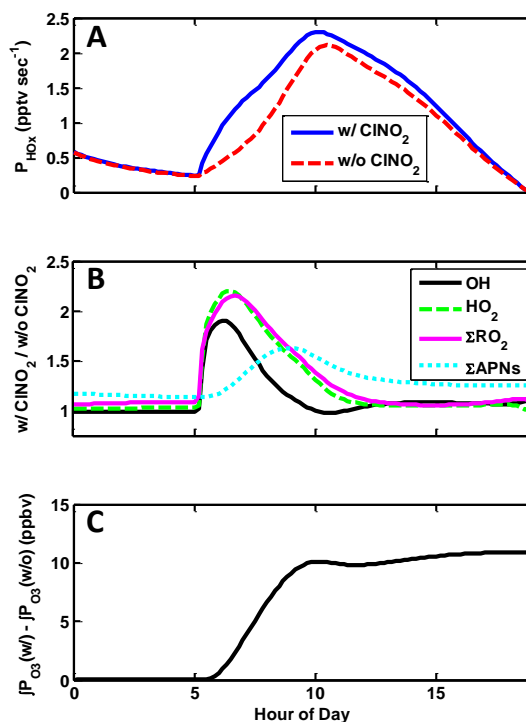


Fig. 5. (A) The HO_x production rate with CINO₂ formation (solid blue line) and without CINO₂ formation (dashed red line). (B) The ratio of the hydroxyl radical (solid black line), hydroperoxyl radical (dashed green line), sum of organic peroxy radicals (solid pink line), and sum of acyl peroxy nitrates (dotted cyan line) for the with-CINO₂ case relative to the without-CINO₂ case. (C) The difference between the integrated ozone production rate with CINO₂ formation and the integrated ozone production rate without CINO₂ formation.

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; Allan et al., 2007). However, the presence of additional Cl· from CINO₂ 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 CINO₂ induced morning perturbations to 25 and 50 % increases in OH and the sum of HO₂ and RO₂, 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 CINO₂ effects on morning oxidant evolution.

CINO₂ formation and photolysis has implications for the reactive nitrogen budget as well. CINO₂ 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 CINO₂ analogous to thermal decomposition

of acyl peroxy nitrates such as APN. In addition to this direct impact on NO_x transport, we find significant perturbations to acyl peroxy nitrate formation to occur in the with-CINO₂ case (see Fig. 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 CINO₂ 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-CINO₂ 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 CINO₂ formation extends the lifetime of NO_x through the night, our model suggests that faster OH + NO₂, 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-CINO₂ than in the without-CINO₂ case.

3.3 Impact on ozone production rate and odd oxygen

We illustrate the influence of CINO₂ chemistry on ozone production in Fig. 5c (also see Fig. S12 in the Supplement). Over the entire model day, the difference between the integrated ozone production rate with 1.5 ppbv CINO₂ and the integrated ozone production rate without CINO₂ is about 12 ppbv. The majority of this enhancement takes place over the first 5 h after sunrise where at 06:30 model time the ozone production rate is enhanced by ~200%. The pre-noon ozone mixing ratios relative to the without-CINO₂ case are increased by ~20% with ~10% increase over the remainder of the day including peak ozone which occurs at about 17:00 model time. Such an influence is potentially large enough to affect attainment of air quality standards in polluted coastal regions where exceedances are often only tens of ppbv over the current standard (Parrish et al., 2010; Qin et al., 2004; US EPA, 2006). The enhancement in ozone production scales nearly linearly with the CINO₂ 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 results in a slightly smaller 9 ppbv enhancement in the integrated ozone production rate due to CINO₂ chemistry.

The above result is also interesting to consider in terms of the impact of nocturnal nitrogen oxide chemistry on the odd-oxygen budget. Defining O_x as the sum of O₃ and NO₂, our model predicts that N₂O₅ reactions on aerosol particles consume 9 ppbv O_x at night. If we neglect CINO₂ formation, this 9 ppbv O_x is permanently lost due to nitrate formation from N₂O₅ hydrolysis. However, incorporating CINO₂ formation, with a yield (branching ratio) of 50%, results in up to 12 ppbv O_x produced the subsequent day compared to the case where CINO₂ formation is neglected. Thus, due to

CINO₂ formation and its daytime impact on oxidants and ozone, nighttime N₂O₅ chemistry does not net destroy O_x but is in fact potentially a net source, or at least a null cycle, for the Los Angeles region conditions we simulate here.

While not directly comparable, our results appear generally consistent with a recent 3-D CMAQ modeling study of CINO₂ effects on ozone and particulate nitrate (Sarwar et al., 2012). In the Los Angeles region, the CMAQ modeling showed roughly a 2–4 ppbv increase in daytime ozone per ppbv CINO₂ photolyzed, with maxima approaching 8 ppbv ppbv⁻¹. Likely important in setting the actual ozone enhancement caused by CINO₂ is, among other possibilities, the extent to which a model mixes background marine air with the polluted core during transport and the model predicted vertical distribution of CINO₂. These issues will be important to test with observations in order to validate model representations of this process.

4 Summary and conclusions

These model results suggest that CINO₂ photolysis is likely a major Cl· source, if not the dominant source, under conditions similar to those sampled in the Los Angeles region during CalNex 2010. The impact of CINO₂ on potential daytime halogen atom recycling is substantial, with significant enhancements predicted on other Cl· reservoirs like ClONO₂, HOCl, and Cl₂. Relative to model runs without CINO₂ formation, the presence of CINO₂ causes significant and non-negligible perturbations in HO_x, RO₂, APN, and ozone production. Relative to a model without CINO₂ formation and heterogeneous HONO production, incorporating CINO₂ perturbed the integrated total radical and ozone production rates by 20%, with perturbations in RO_x and APN > 100%. Moreover, we show that, given these effects, the impact of N₂O₅ reactions on aerosol particles is not a net sink of odd oxygen but instead a net source for 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 CINO₂ will ultimately depend upon the presence of HONO and the abundance of CINO₂ and HONO vertically as well as seasonally.

We conclude by noting that during winter, in locations such as the northeastern US, the role of CINO₂ may be substantially more important to the total radical budget given that O(¹D) production and H₂O 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 CINO₂ approaches similar concentrations (Kercher et al., 2009). This idea is consistent with the apparently important role of CINO₂ at inland locations during wintertime as illustrated by recent studies at the Uintah Basin, Utah (Edwards et al., 2013).

Supplementary material related to this article is available online at <http://www.atmos-chem-phys.net/14/3789/2014/acp-14-3789-2014-supplement.pdf>.

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