

## Modeling heterogeneous ClNO<sub>2</sub> formation, chloride availability, and chlorine cycling in Southeast Texas

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### ABSTRACT

Nitryl Chloride (ClNO<sub>2</sub>) mixing ratios above 1 ppbv have been measured off the coast of Southeast Texas. ClNO<sub>2</sub> formation, the result of heterogeneous N<sub>2</sub>O<sub>5</sub> uptake on chloride-containing aerosols, has a significant impact on oxidant formation for the Houston area. This work reports on the modeling of ClNO<sub>2</sub> formation and describes the sensitivity of ClNO<sub>2</sub> formation to key parameters. Model sensitivity analyses found that: (1) Chloride availability limits the formation of nitryl chloride at ground level but not aloft; (2) When excess particulate chloride was assumed to be present at ground level through sea salt, ClNO<sub>2</sub> concentrations increased in some locations by a factor of 13, as compared to cases where sea salt chloride was assumed to be limited; (3) Inland formation of ClNO<sub>2</sub> seems feasible based on chloride availability and could have a large impact on total ClNO<sub>2</sub> formed in the region; and (4) ClNO<sub>2</sub> formation is quite sensitive to the assumed yield of ClNO<sub>2</sub> from N<sub>2</sub>O<sub>5</sub> uptake. These results demonstrate that there is a need for further field studies to better understand the geographic extent of ClNO<sub>2</sub> formation and the atmospheric conditions which control partitioning of chloride into the particle phase. In addition, this work examined the role of ClNO<sub>2</sub> in the cycling of chlorine between chloride and reactive chlorine radicals. The modeling indicated that the majority of reactive chlorine in Texas along the Gulf coast is cycled through ClNO<sub>2</sub>, demonstrating the importance of including ClNO<sub>2</sub> into photochemical models for this region.

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### 1. Introduction

Ambient measurements of Nitryl Chloride (ClNO<sub>2</sub>) were made for the first time during the TexAQS II/GoMACCS field campaign in 2006 (Osthoff et al., 2008). ClNO<sub>2</sub> mixing ratios measured on board the Research Vessel Ronald H Brown reached over 1 part per billion by volume (ppbv) off the coast of southeast Texas. This compound is potentially significant for several reasons. First, ClNO<sub>2</sub> serves as a NO<sub>x</sub> reservoir at night which prevents nitrogen from being lost to inactive forms such as nitric acid. Second, ClNO<sub>2</sub> represents a largely

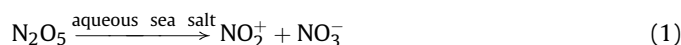
unstudied form of chlorine in the atmosphere that may be a key step in a pathway that converts particulate chloride into reactive chlorine radicals. The effect of this chemistry on both NO<sub>x</sub> and chlorine cycling has the potential to increase ozone production in regionally polluted areas (Simon et al., 2009; Osthoff et al., 2008).

Finlayson-Pitts et al. (1989) first suggested that ClNO<sub>2</sub> could form from heterogeneous reactions between N<sub>2</sub>O<sub>5</sub> and aqueous sea salt aerosols. Osthoff et al. (2008) showed strong temporal correlations between ClNO<sub>2</sub> and N<sub>2</sub>O<sub>5</sub> concentrations measured in the Gulf of Mexico. Their results make a compelling case that the dominant mechanism for nitryl chloride formation is this heterogeneous pathway. Studies that have investigated heterogeneous ClNO<sub>2</sub> formation in the laboratory suggest that the mechanism is the same as that of heterogeneous N<sub>2</sub>O<sub>5</sub> hydrolysis [Reaction (1)] (Behnke et al., 1997; Schweitzer et al., 1998).

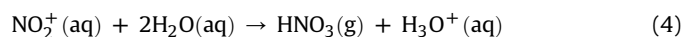
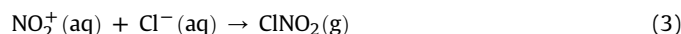
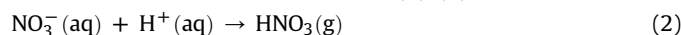
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The  $\text{Cl}^-$  ions in aqueous aerosol compete with  $\text{H}_2\text{O}$  to react with  $\text{NO}_2^+$ . Therefore the reaction can either result in  $2\text{HNO}_3$  or  $\text{ClNO}_2 + \text{HNO}_3$  as shown in Reactions (2)–(4).



The yield of nitryl chloride from this reaction [i.e. the fraction of  $\text{NO}_2^+$  ions that proceed to Reaction (3) instead of Reaction (4)] is strongly dependent on the chloride ion concentration in the aerosol (Behnke et al., 1997; Roberts et al., in press; Schweitzer et al., 1998; Thornton and Abbatt, 2005). Yields close to 1 at high molarities (1 M) suggest that  $\text{Cl}^-$  ions outcompete  $\text{H}_2\text{O}$  as discussed in Section 3.2.3. In fact, both Behnke et al. (1997) and Roberts et al. (in press) report nitryl chloride formation on aerosols as dilute as 0.01 M. Most laboratory studies are in relative agreement on their measurements of reactive uptake coefficients for  $\text{N}_2\text{O}_5$  on chloride aerosols (0.01–0.03) (Behnke et al., 1997; Schweitzer et al., 1998; Thornton and Abbatt, 2005).

Previous articles have described the impact of  $\text{ClNO}_2$ , once formed, on ozone formation (Simon et al., 2009; Osthoff et al., 2008). The work presented here incorporated heterogeneous  $\text{ClNO}_2$  formation on ambient aerosol, as well as other related heterogeneous  $\text{N}_2\text{O}_5$  chemistry, and investigated the sensitivity of  $\text{ClNO}_2$  formation to various model parameters. Specifically, this work studies the dependence of  $\text{ClNO}_2$  formation on available chloride and its sensitivity to the assumed yield of  $\text{ClNO}_2$ . Finally, the implications of this chemistry for chlorine cycling and the total reactive chlorine budget in Southeast Texas are investigated.

## 2. Methods

### 2.1. Photochemical simulations

Photochemical modeling was performed using the Comprehensive Air quality Model with extensions (CAMx) version 4.2 (Environ,

2008). This program is a three-dimensional Eulerian model which calculates the effects of emissions, chemistry, deposition, advection, and dispersion on chemical concentrations in the atmosphere. A full description of the model treatment of these processes as well as the nesting schemes and numerical solvers can be found in the CAMx User's Guide (Environ, 2008). Evaluations of CAMx model performance have been carried out by Tesche et al. (2006) and Morris et al. (2005). CAMx was chosen for this work to facilitate comparison with previous studies of chlorine and nitryl chloride in the Houston area (Chang and Allen, 2006a,b; Wang et al., 2007; Simon et al., 2009).

The modeling domain consisted of three two-way nested grids, as shown in Fig. 1. The two largest of these grids had cells with horizontal dimensions of 36 km by 36 km and 12 km by 12 km. These two grids have 17 vertical layers covering the lowest 15 km of the atmosphere. The finest of the grids, which was centered over the Houston area, had cells with horizontal dimensions of 4 km by 4 km and 28 vertical layers covering the lowest 15 km of the atmosphere. The layers are more finely divided at lower altitudes, with 12 of the 28 layers in the lowest 1000 m. A full description of the thickness of each vertical layer is described by the Texas Commission on Environmental Quality for their SIP mid-course review modeling ([http://www.tceq.state.tx.us/implementation/air/airmod/data/hgb1\\_camx\\_domain.html](http://www.tceq.state.tx.us/implementation/air/airmod/data/hgb1_camx_domain.html)). The model simulation was run for the dates of August 30, 2006 through September 9, 2006, one of the time periods when the *R.V. Ronald H. Brown* was taking measurements in the Houston area. August 28 and 29 were used as model spin-up days. Meteorological inputs for the modeled days were developed at the University of Houston (Ngan, 2008), as described by Simon et al. (2009) and in the supplemental information.

Emissions inputs for ozone precursor compounds ( $\text{NO}_x$  and VOCs) are described by Simon et al. (2009). In addition, emissions of anthropogenic  $\text{Cl}_2$ , primary particulate matter (PM),  $\text{SO}_2$ , and ammonia were included in the modeling. A full description of these emissions and the associated boundary conditions can be found in the supplemental information.

### 2.2. Updated model chemistry

Current versions of the CAMx software include a standard CB IV chemical mechanism (Gery et al., 1989), and two enhanced mechanisms: one with added chlorine chemistry described in Tanaka et al.

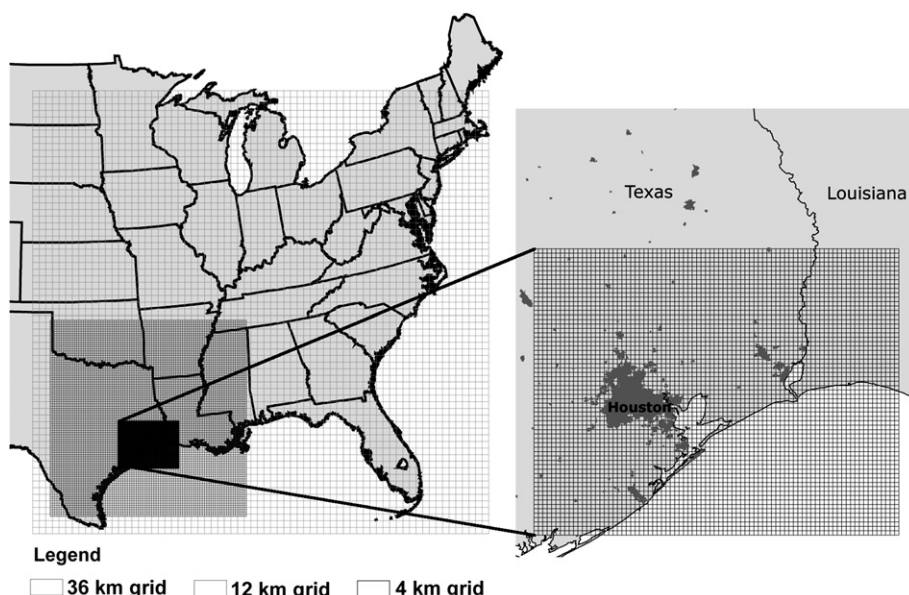


Fig. 1. Nested domains used in CAMx modeling.

(2003) and one with added aerosol chemistry based on work by Pandis et al. (1993), Nenes et al. (1998), and Yarwood et al. (2005). The aerosols in this model are categorized into 16 main species (sulfate, nitrate, ammonium, water, 9 secondary organic aerosol species, sodium, chloride, primary organic matter, elemental carbon, and 4 non-reactive species) and 4 size bins (0.039–0.156  $\mu\text{m}$ ; 0.156–0.625  $\mu\text{m}$ ; 0.625–2.5  $\mu\text{m}$ ; and 2.5–10  $\mu\text{m}$ ). Since this study entails modeling processes that interact both with chlorine and with aerosols, the chlorine and aerosol chemistry were linked in a single mechanism.

To correctly model the heterogeneous conversion of  $\text{N}_2\text{O}_5$  to  $\text{ClNO}_2$ , there are several key factors that must be properly accounted for: the formation of  $\text{NO}_3$  from  $\text{O}_3 + \text{NO}_2$ , the strongly temperature-dependant reversible inter-conversion of  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$ , and the relative magnitudes of  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  losses. The formation and destruction reactions of  $\text{NO}_3$  are handled in CAMx's standard CB IV chemical mechanism. The reactions of  $\text{N}_2\text{O}_5$  are also, for the most part, included in the standard chemical mechanism. A major uncertainty in the  $\text{N}_2\text{O}_5$  chemistry in CAMx is the loss mechanisms for  $\text{N}_2\text{O}_5$  (both homogeneous and heterogeneous). Field measurements suggest that gas-phase reactions of  $\text{N}_2\text{O}_5$  are not a significant loss pathway in the lower troposphere in southeast Texas (Brown et al., 2006, 2009; Simon, 2008), so gas-phase hydrolysis of  $\text{N}_2\text{O}_5$  was not included in the model simulations. Changes to the heterogeneous chemistry used in this modeling are discussed below.

The heterogeneous loss rate for  $\text{N}_2\text{O}_5$  was calculated using Equation (5) and the heterogeneous formation rate of  $\text{ClNO}_2$  was calculated using Equation (6),

$$\frac{-d[\text{N}_2\text{O}_5]}{dt} = k[\text{N}_2\text{O}_5] = \frac{\gamma\omega A}{4}[\text{N}_2\text{O}_5] \quad (5)$$

$$\frac{d[\text{ClNO}_2]}{dt} = Yk[\text{N}_2\text{O}_5] = \frac{Y\gamma\omega A}{4}[\text{N}_2\text{O}_5] \quad (6)$$

where  $k$  ( $\text{s}^{-1}$ ) is the first order rate constant for the heterogeneous reaction,  $Y$  is the yield of  $\text{ClNO}_2$  for each molecule of  $\text{N}_2\text{O}_5$  reacted,  $\gamma$  is the reactive uptake coefficient (the probability that a molecule

of  $\text{N}_2\text{O}_5$  which impacts a particle will react),  $\omega$  ( $\text{m s}^{-1}$ ) is the mean molecular speed of the  $\text{N}_2\text{O}_5$ , and  $A$  ( $\text{m}^2 \text{m}^{-3}$  of air) is the total aerosol surface area. For each time step, the total aerosol surface area was calculated based on model predictions of speciated aerosol mass in each grid cell. For this calculation, particles were assumed to be spherical with species-specific densities given by Simon (2008). The assumption of spherical particles is reasonable since previous studies in Texas have shown aerosol to be predominantly in a deliquesced state (Santarpia et al., 2004). Mean particle diameters were taken as the geometric mean for each of four PM size bins used. It should be noted that Equations (5) and (6) represent the change in  $\text{N}_2\text{O}_5$  and  $\text{ClNO}_2$  concentrations from this specific chemistry and not the full differential equation with all source and loss terms.

The reactive uptake coefficient is a complex function of aerosol composition and relative humidity (Davis et al., 2008; Evans and Jacob, 2005). A recent study of  $\text{N}_2\text{O}_5$  reactivity in Texas showed that parameterization of  $\gamma(\text{N}_2\text{O}_5)$  based on laboratory studies are systematically larger than direct determinations from aircraft measurements taken over inland areas during night flights (Brown et al., 2009). However,  $\text{N}_2\text{O}_5$  and  $\text{ClNO}_2$  data from ship based measurements in Galveston Bay and other location along the Gulf Coast were consistent with relatively larger  $\gamma(\text{N}_2\text{O}_5)$ , in the range of 0.02–0.03 (Osthoff et al., 2008). On the basis of these empirical observations, geographic location was used as a surrogate for  $\gamma(\text{N}_2\text{O}_5)$  in this study. Heterogeneous chemistry was only included in the 4 and 12 km modeling domain, since the focus of this modeling is to evaluate chemistry in Southeast Texas. Because model parameters were based on local ambient measurements, the chosen modeling setup may not be applicable to other areas of the country. The 4 and 12 km domains were split into 3 regions (see Fig. 2): region 1 covered all marine and coastline grid cells, region 2 covered the Houston Ship Channel, and region 3 covered all other terrestrial grid cells. Although region 2 is small in area it was treated as a distinct region because it includes a large number of industrial sources. Heterogeneous  $\text{N}_2\text{O}_5$  uptake was modeled using Reactions (7)–(9) for regions 1, 2, and 3 respectively. It should be

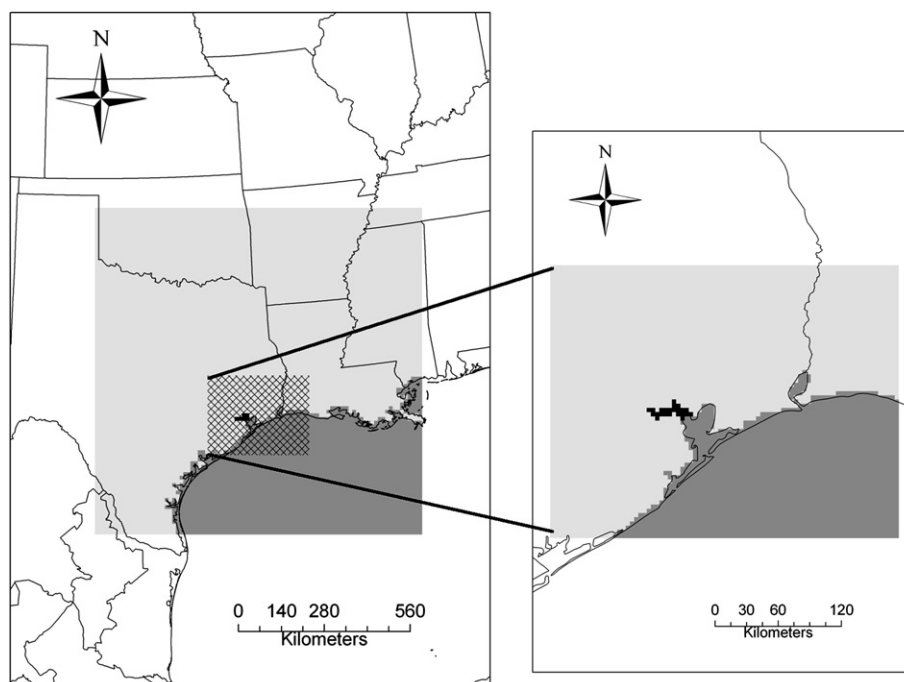
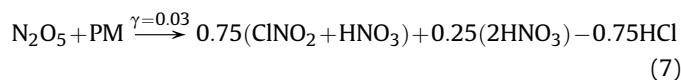


Fig. 2. Regions used to define heterogeneous  $\text{N}_2\text{O}_5$  reaction rate parameters. Region 1 is shown in dark gray, region 2 is shown in black, and region 3 is shown in light gray.

noted that water as a reactant is implied in these reactions, but is not explicitly shown.



Aldener et al. (2006) reported a reactive uptake of 0.03 from ambient measurements taken in the marine boundary layer. In addition, Osthoff et al. (2008) modeled data using a  $\gamma(\text{N}_2\text{O}_5)$  value of 0.025 for the TexAQs 2006 episode. Based on these two studies, the reactive uptake coefficient for Reaction (7) was set to 0.03. Reaction (7) represents a 75% yield of  $\text{ClNO}_2$  with respect to  $\text{N}_2\text{O}_5$  uptake. Osthoff et al. (2008) reported yields from measurements in the Gulf of Mexico of between 18% and 100%. The 75% yield is an intermediate value; however, the sensitivity of the model to this value is tested in this work. Reaction (7) was added as a loss mechanism for HCl, since one chlorine atom is required to form each  $\text{ClNO}_2$  molecule. Given that CAMx calculates a rapid equilibrium between gas-phase HCl and particle-phase chloride, removing the HCl from the gas phase is essentially equivalent to removing it from the particle phase. Reaction (7) was shut off [and  $\text{N}_2\text{O}_5$  chemistry switched to Reaction (9)] when HCl mixing ratios dropped below 0.5 parts-per trillion by volume (pptv) to prevent creation of chlorine mass. This threshold was taken as 0.1% of a typical HCl concentration for the Houston area (0.5 ppbv) as reported by Chang and Allen (2006b) and is assumed to be a lower bound for the concentration of chloride required to form  $\text{ClNO}_2$ . This will give an upper-bound on the amount of  $\text{ClNO}_2$  formed since the model uses a constant yield until HCl concentrations reach this threshold, while actual yields decrease at lower particulate chloride concentrations. The uncertainties due to this assumption and the assumption of a constant 75% yield are discussed in more detail below.

The reactive uptake coefficients in Regions 2 and 3 were based on measurements made by Brown et al. (2009) and Brown et al. (2006). The reactive uptake coefficient for region 2, an area characterized by non-neutralized sulfate aerosols, was set at the upper end of the ambient measured values (0.01). The reactive uptake coefficient for region 3, whose aerosol is composed of neutralized ammonium sulfate and secondary organic aerosol, was set at the lower end of the measured range (0.001). It is assumed that over terrestrial grid cells, chloride availability is low and a negligible

amount of  $\text{ClNO}_2$  will form in these locations. However, the sensitivity of the model to this assumption is evaluated below.

The final change made to the chemical mechanism in CAMx was the addition of the photolysis of  $\text{ClNO}_2$  to form  $\text{NO}_2$  and  $\text{Cl}^\bullet$  as described in Simon et al. (2009).

### 3. Results

#### 3.1. Model predictions of $\text{N}_2\text{O}_5$ , $\text{ClNO}_2$ , and $\text{HNO}_3$ mixing ratios

Maximum and average hourly ground-level mixing ratios of  $\text{N}_2\text{O}_5$ ,  $\text{ClNO}_2$ , and  $\text{HNO}_3$  in the 4 km domain are shown in Table 1. The values were calculated for each night in the simulation for the hours of 10pm–5am. Average values for  $\text{ClNO}_2$  mixing ratios are reported only over marine grid cells where formation occurs in the model. Maximum predicted  $\text{ClNO}_2$  mixing ratios ranged from 256 pptv to 1210 pptv on different nights. The maximum 1-min average  $\text{ClNO}_2$  mixing ratio measured aboard the *Research Vessel Ronald H Brown* during the TexAQs II/GoMACCS field study was just above 1300 pptv, similar to the maximum  $\text{ClNO}_2$  concentrations in the model. More detailed comparisons between model predictions and ambient measurements for PM surface area,  $\text{N}_2\text{O}_5$ ,  $\text{HNO}_3$ , and  $\text{ClNO}_2$  mixing ratios are given in the supplemental information. These comparisons show that predicted values using this modeling scheme are generally consistent with measured values, except in the Houston Ship Channel, where  $\text{ClNO}_2$  concentrations are consistent with measurements and  $\text{N}_2\text{O}_5$  is over-predicted. Inaccuracies in this region are likely due to uncertainties in the emissions inventory or sub-grid cell phenomena associated with localized plumes.

Fig. 3 shows the spatial distribution of the species on the night of Aug 30–Aug 31, 2006. The spatial distribution of  $\text{N}_2\text{O}_5$  depends on the location of  $\text{NO}_x$  in urban and industrial plumes. The major  $\text{NO}_x$  plumes on every night originated from Houston, TX, Beaumont, TX, and Lake Charles, LA. PM surface area was also highest in these three urban/industrial areas. The spatial distribution  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  mixing ratios were the same, which is expected since there is rapid inter-conversion between these two compounds in the model.  $\text{HNO}_3$  and  $\text{ClNO}_2$  follow the same spatial patterns as  $\text{N}_2\text{O}_5$  except for the fact that  $\text{ClNO}_2$  was mostly restricted to marine and near-marine grid cells. For the Houston area, it appears that the  $\text{NO}_x$  and aerosol surface area are highest in the source region, while  $\text{N}_2\text{O}_5$ ,  $\text{ClNO}_2$ , and  $\text{HNO}_3$  are highest downwind. This pattern is to be expected at night since  $\text{NO}_2$  reacts with ozone to form  $\text{NO}_3$  and eventually  $\text{N}_2\text{O}_5$ . Therefore the  $\text{NO}_2$  is generally observed in fresh plumes and the  $\text{N}_2\text{O}_5$  and its reaction products reach peak concentrations several hours downwind of the source region.

**Table 1**

Average and Maximum ground-level concentrations for  $\text{N}_2\text{O}_5$ ,  $\text{ClNO}_2$ , and  $\text{HNO}_3$  for nights in the modeled episode in the 4 km domain.

| Night of:     | $\text{N}_2\text{O}_5$ (pptv) |         | $\text{ClNO}_2$ (pptv) |         | $\text{HNO}_3$ (pptv) |         |
|---------------|-------------------------------|---------|------------------------|---------|-----------------------|---------|
|               | Average                       | Maximum | Average <sup>a</sup>   | Maximum | Average               | Maximum |
| Aug 30–Aug 31 | 78                            | 3885    | 14                     | 419     | 719                   | 3338    |
| Aug 31–Sep 1  | 280                           | 8526    | 85                     | 1034    | 1519                  | 6297    |
| Sep 1–Sep 2   | 304                           | 8016    | 81                     | 1210    | 1830                  | 9675    |
| Sep 2–Sep 3   | 189                           | 8906    | 37                     | 362     | 1000                  | 6286    |
| Sep 3–Sep 4   | 191                           | 7362    | 51                     | 256     | 1039                  | 6113    |
| Sep 4–Sep 5   | 92                            | 4565    | 31                     | 400     | 677                   | 4415    |
| Sep 5–Sep 6   | 18                            | 2235    | 17                     | 276     | 459                   | 1946    |
| Sep 6–Sep 7   | 199                           | 6215    | 101                    | 1002    | 937                   | 7260    |
| Sep 7–Sep 8   | 316                           | 8165    | 97                     | 911     | 1995                  | 16 025  |
| Sep 8–Sep 9   | 333                           | 13 547  | 161                    | 882     | 2620                  | 13 964  |

<sup>a</sup> Average values for  $\text{ClNO}_2$  were only calculated for marine grid cells.



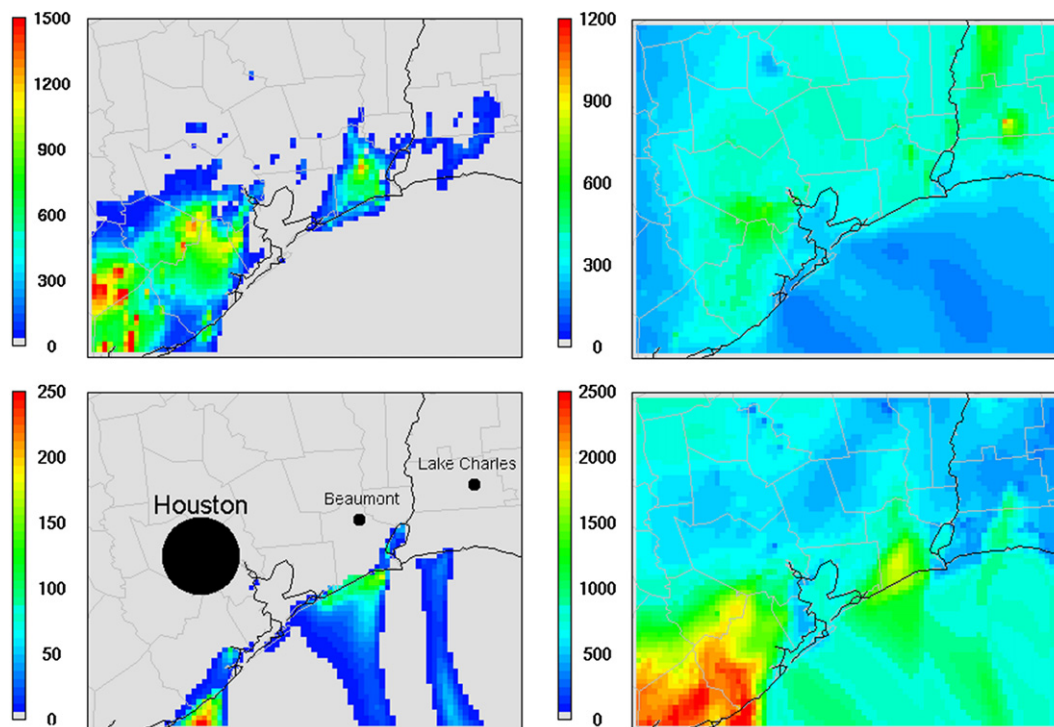


Fig. 3. Pollutant concentrations at 4am on Aug 31, 2006:  $\text{N}_2\text{O}_5$  (pptv) at upper left, aerosol surface area ( $\mu\text{m}^2 \text{cm}^{-3}$ ) at upper right,  $\text{ClNO}_2$  (pptv) at lower left,  $\text{HNO}_3$  (pptv) at lower right.

### 3.2. Evaluation of chloride availability and its effect on $\text{ClNO}_2$ production

Even with data from measurements taken during TexAQS II, there is still a great deal of uncertainty about parameters used to model heterogeneous  $\text{N}_2\text{O}_5$  chemistry. One key uncertainty is the availability of chloride. This can affect the  $\text{ClNO}_2$  yield from heterogeneous  $\text{N}_2\text{O}_5$  uptake and the geographic extent of these reactions. A set of sensitivity runs was performed to further evaluate the assumptions about chloride availability that were made in this model simulation.

#### 3.2.1. Effect of using the HCl switch

The methods described above include techniques implemented to account for the depletion of HCl due to  $\text{ClNO}_2$  formation and for the fact that heterogeneous uptake will not result in  $\text{ClNO}_2$  formation unless there is particulate chloride present. The two elements of this technique were 1) the loss of an HCl molecule for every  $\text{ClNO}_2$  molecule formed [see Reaction (7)] and 2) an “HCl switch” (based on the assumption that gas-phase and particulate chloride are rapidly exchanged). When the gas-phase HCl, and therefore total chloride, concentration dropped below a minimum level (0.5 pptv) all  $\text{ClNO}_2$  formation was turned off. Further evaluation of the sensitivity of the model to this “HCl switch” chemistry can give insight into how chloride limitation is affecting the heterogeneous  $\text{N}_2\text{O}_5$  chemistry. Two sensitivity runs are used to evaluate this dependency further.

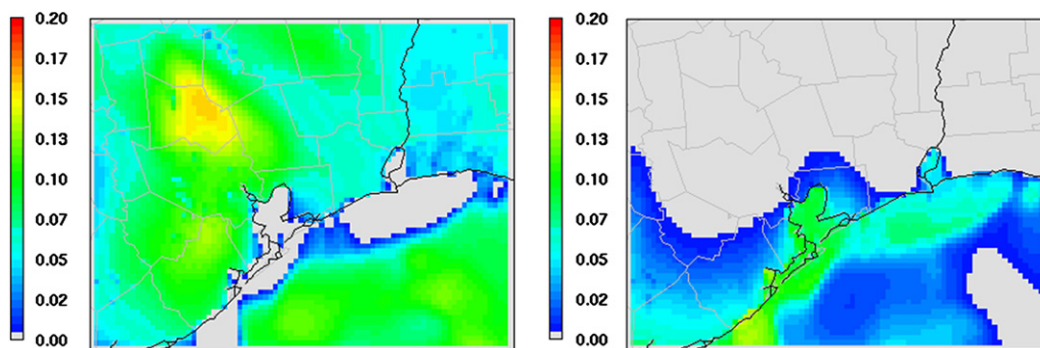
**3.2.1.1.  $\text{ClNO}_2$  formation in the presence of excess chloride.** In this sensitivity run,  $\text{ClNO}_2$  formation was modeled as if it were not dependent on chloride availability. To do this, the “HCl switch” was always on. There was no loss of HCl when  $\text{ClNO}_2$  formed and  $\text{ClNO}_2$  formation depended solely on location ( $\text{ClNO}_2$  formation was still restricted to marine grid cells), surface area concentration, and  $\text{N}_2\text{O}_5$  mixing ratio, and not on the predicted HCl mixing ratio.

Results from this run indicate how much  $\text{ClNO}_2$  would form if there were a surplus of chloride present in the atmosphere.

This run shows significant increases in HCl mixing ratios in areas where  $\text{ClNO}_2$  is present. Fig. 4 shows the predicted HCl mixing ratios on September 1, 2006 at 5am in the base case simulation and the predicted increases in HCl caused by eliminating HCl loss due to  $\text{ClNO}_2$  formation. In regions where HCl mixing ratios were essentially zero in the main run, HCl mixing ratios increase by up to 0.4 ppbv in this run. Fig. 4 demonstrates that the model predicts  $\text{ClNO}_2$  formation will almost completely deplete chloride concentrations in the locations where it occurs. The fact that  $\text{ClNO}_2$  formation continues to occur throughout the night in the base case simulation is likely due to sea salt emissions, which act as a continual source of chloride.

Ground-level nitryl chloride mixing ratios increased significantly in this sensitivity analysis. On some days, the maximum ground-level nitryl chloride mixing ratio increased by more than a factor of three. The  $\text{ClNO}_2$  mixing ratio in a single ground-level grid cell increased by up to 3200 pptv (more than a tenfold increase). In addition, some decreases in  $\text{ClNO}_2$  mixing ratios occurred in this sensitivity run. The maximum decrease was almost 300 pptv. These decreases may be caused by faster depletion of  $\text{N}_2\text{O}_5$  when the  $\text{ClNO}_2$  formation is not limited by chloride availability. Fig. 5 shows the  $\text{ClNO}_2$  mixing ratio in the base case heterogeneous chemistry run at 5am on September 1, 2006 as well as the changes in  $\text{ClNO}_2$  mixing ratios that occurred in the simulation with no chloride limitations. The spatial distribution of the changes in  $\text{ClNO}_2$  mixing ratios is similar to the distribution of depleted HCl mixing ratios shown in Fig. 4. Also, the spatial extent of the  $\text{ClNO}_2$  did not change significantly, only the magnitude of the mixing ratios. Table 2 summarizes the changes that occurred in ground-level HCl and  $\text{ClNO}_2$  mixing ratios in this simulation versus the base case simulation.

In addition to the ground-level mixing ratio, vertical profiles were also evaluated for this simulation. Figs. 6 and 7 show the vertical profile of maximum and average  $\text{ClNO}_2$  mixing ratios in the 4 km domain at 1am for 4 nights. These figures show that on many nights



**Fig. 4.** HCl mixing ratio (ppbv) in base case run on September 1, 2006 at 5am (left). Change in HCl mixing ratio (ppbv) caused by not depleting HCl when CINO<sub>2</sub> is formed on September 1, 2006 at 5am (right).

CINO<sub>2</sub> mixing ratios above 1000 m are virtually identical in the base case heterogeneous chemistry run and in the sensitivity run: August 31 (shown), September 1 (shown), September 2 (shown), September 3 (not shown), September 5 (not shown), and September 9 (not shown). On those nights, marine chloride availability appears to play no role in limiting CINO<sub>2</sub> formation above 1000 m. Since most chloride is emitted at ground-level, it might be expected that chloride would be most concentrated at lower altitudes and that this would be a main limiting factor for CINO<sub>2</sub> formation aloft. However, these results suggest that the opportunity for interaction between N<sub>2</sub>O<sub>5</sub> and particle surfaces is the limiting factor for CINO<sub>2</sub> formation aloft.

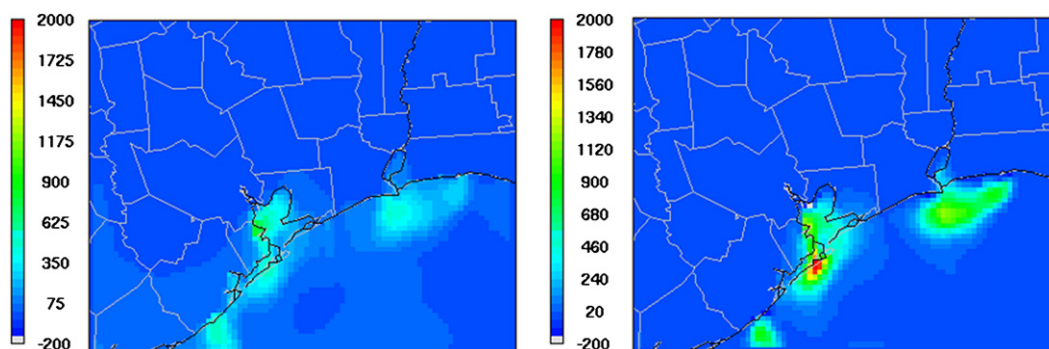
Based on this simulation, marine chloride availability greatly affected the magnitude of CINO<sub>2</sub> mixing ratios at ground-level (by up to a factor of 13), but not aloft. In addition, horizontal spatial distributions were not affected within the marine grid cells. The sensitivity run described in the next section tests the chloride availability inland and gives insight into whether sufficient chloride is present over terrestrial regions to lead to significant CINO<sub>2</sub> formation.

**3.2.1.2. Allowing CINO<sub>2</sub> formation at inland locations.** In this sensitivity run, the “HCl switch” was used for the entire 4 km and 12 km domains instead of just for the marine grid cells. CINO<sub>2</sub> formation (Reaction (7)) proceeded wherever HCl mixing ratios were sufficiently high (above 0.5 pptv) regardless of whether the location was marine or terrestrial. The reactive uptake and yield used were the same as described above. When HCl dropped below 0.5 pptv, Reaction (8) was used in the Houston Ship Channel grid cells and Reaction (9) was used in all other cells. Previous modeling limited the geographic extent of CINO<sub>2</sub> formation based on the assumption that it would only occur in a marine environment where sea salt emissions are prevalent. This run eliminated that constraint, so that

CINO<sub>2</sub> could form inland wherever HCl mixing ratios were high enough. There have been no inland measurements of CINO<sub>2</sub> in the Houston area, so model results cannot be compared at this time with ambient data.

Fig. 8 shows comparisons of CINO<sub>2</sub> mixing ratios in the base case run and in the sensitivity run which allowed formation at inland locations on the evening of September 4, 2006. This figure shows that the model predicts sufficient concentrations of chloride inland to form CINO<sub>2</sub>. In this sensitivity run, CINO<sub>2</sub> mixing ratios were often above 400 pptv over the city of Houston. CINO<sub>2</sub> mixing ratios over land that was within 50 km of the shoreline were often as high as mixing ratios over marine grid cells. On some days, CINO<sub>2</sub> mixing ratios above 100 pptv were predicted at locations more than 100 km inland.

Table 3 summarizes changes in domain-wide maximum ground-level CINO<sub>2</sub> mixing ratios and domain-wide CINO<sub>2</sub> mass at 5am. On some days the maximum CINO<sub>2</sub> mixing ratio was greater in the base case heterogeneous chemistry run and on some days the maximum mixing ratios were greater in this sensitivity run. It appears that when mixing ratios were greater in the base case heterogeneous chemistry run, the maxima usually occurred where a NO<sub>x</sub> plume first came in contact with marine grid cells. In the sensitivity run where CINO<sub>2</sub> formation could occur over land, the N<sub>2</sub>O<sub>5</sub> in the NO<sub>x</sub> plume became partially depleted over land so the CINO<sub>2</sub> mixing ratios were lower but covered a greater area. In contrast, in the base case heterogeneous chemistry run the NO<sub>x</sub> plumes stayed relatively concentrated over land and when these plumes suddenly contacted the marine environment, a great deal of CINO<sub>2</sub> was formed all at once, causing intense peaks over small areas. This was due to the fact that the model predicted a lower reactive uptake coefficient over terrestrial grid cells when no chloride was present (0.001) versus when sufficient chloride is available to form CINO<sub>2</sub> (0.03).



**Fig. 5.** CINO<sub>2</sub> mixing ratio (pptv) in base case run on September 1, 2006 at 5am (left). Change in CINO<sub>2</sub> mixing ratio (pptv) when excess chloride is present on September 1, 2006 at 5am (right).

**Table 2**Summary of changes in ClNO<sub>2</sub> and HCl concentrations when excess chloride is present.

| Night of:    | Max ClNO <sub>2</sub> concentration in main run (pptv) | Max ClNO <sub>2</sub> concentration with excess chloride (pptv) | Max ClNO <sub>2</sub> increase in a single grid cell <sup>a</sup> (pptv) | Max ClNO <sub>2</sub> increase in a single grid cell <sup>b</sup> (%) | Max change in HCl in a single grid cell <sup>c</sup> (ppbv) |
|--------------|--|---|--|---|---|
| Aug 30–31    | 419  | 928   | 630  | 210   | 0.2   |
| Aug 31–Sep 1 | 1034   | 2606  | 2020   | 670   | 0.1   |
| Sep 1–2      | 1210   | 3733  | 3244   | 1110  | 0.3   |
| Sep 2–3      | 362  | 800   | 500  | 220   | 0.1   |
| Sep 3–4      | 256  | 817   | 615  | 470   | 0.4   |
| Sep 4–5      | 400  | 996   | 616  | 200   | 0.1   |
| Sep 5–6      | 276  | 397   | 242  | 280   | 0.2   |
| Sep 6–7      | 1002   | 1716  | 1115   | 610   | 0.2   |
| Sep 7–8      | 911  | 2535  | 2216   | 1270  | 0.3   |
| Sep 8–9      | 882  | 1343  | 901  | 390   | 0.4   |

<sup>a</sup> Change in ClNO<sub>2</sub> concentration calculated as concentration in sensitivity run simulation (excess chloride) minus concentration in base case run.<sup>b</sup> Percent increases only calculated for grid cells in which the ClNO<sub>2</sub> concentration was greater than 50 pptv in the sensitivity run simulation.<sup>c</sup> Calculations done between the hours of 8pm and 5am.

This phenomenon can be seen in the Lake Charles, LA plume in Fig. 8. The results reported here show that integrated ClNO<sub>2</sub> is larger in the sensitivity run, even though ClNO<sub>2</sub> mixing ratios may be lower in marine hotspots and that ClNO<sub>2</sub> formation becomes NO<sub>x</sub> limited in the sensitivity run. On days when the maximum ClNO<sub>2</sub> mixing ratio was greater in the sensitivity run, it appears that the maximum occurred over land. This can be seen in Fig. 8, which shows ClNO<sub>2</sub> hotspots over Houston in the sensitivity run but not in the base case heterogeneous chemistry run. The total ClNO<sub>2</sub> mass in the 4 km domain was significantly greater (between a factor of 3 and 22 greater depending on the day) when ClNO<sub>2</sub> formation was allowed to occur over land. This indicates that ClNO<sub>2</sub> formation over land uses reservoirs of chloride that would not be accessed if ClNO<sub>2</sub> formation were restricted to marine cells and again supports the finding that integrated ClNO<sub>2</sub> is larger when inland formation is included in the simulation.

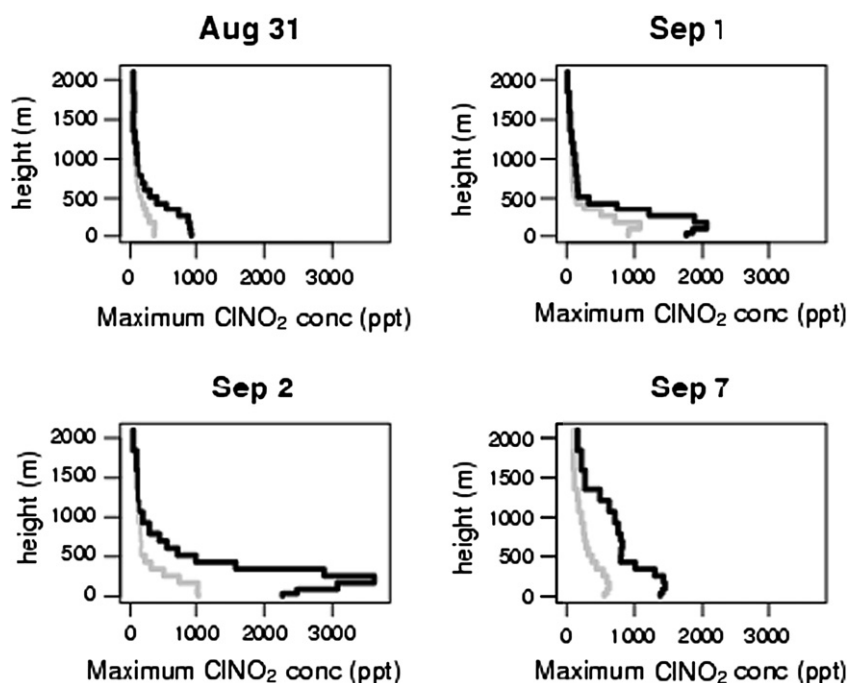
Overall, this sensitivity run predicts that inland chloride concentrations are indeed high enough to form ClNO<sub>2</sub>. Inland formation is important for correctly predicting the magnitude and extent of ClNO<sub>2</sub>

mixing ratios. In addition, a great deal more chloride mass will be converted to ClNO<sub>2</sub> when inland formation is taken into account. Ambient measurements are still needed to verify these model results. It should be noted again that these results represent an upper-bound estimate for ClNO<sub>2</sub> formation since modeled yields were held constant at 75% but actual yields will decrease as HCl concentrations drop.

### 3.2.2. Sensitivity to changes in ClNO<sub>2</sub> yield

The modeling performed above used a ClNO<sub>2</sub> yield in Reaction (7) of 75%. As discussed previously, laboratory studies have shown that this yield depends on the chloride concentration in the aerosol (Behnke et al., 1997; Schweitzer et al., 1998; Roberts et al., in press). Measurements and modeling results reported by Osthoff et al. (2008), show that in the Gulf of Mexico this yield can range from 18% to 100%. Two further modeling runs were performed (one with a 100% yield and one with an 18% yield) to evaluate the upper and lower bounds of ClNO<sub>2</sub> yield for this region.

Table 4 shows the maximum ground-level mixing ratio changes in a single grid cell for ClNO<sub>2</sub> in the low and high yield sensitivity



**Fig. 6.** Vertical profiles of maximum ClNO<sub>2</sub> mixing ratios (pptv) at 1am in the 4 km domain for the base case run (gray) and the sensitivity run with excess chloride (black). Maximum is reported as the maximum concentration at each height (this value may occur in different grid cells in different vertical layers).

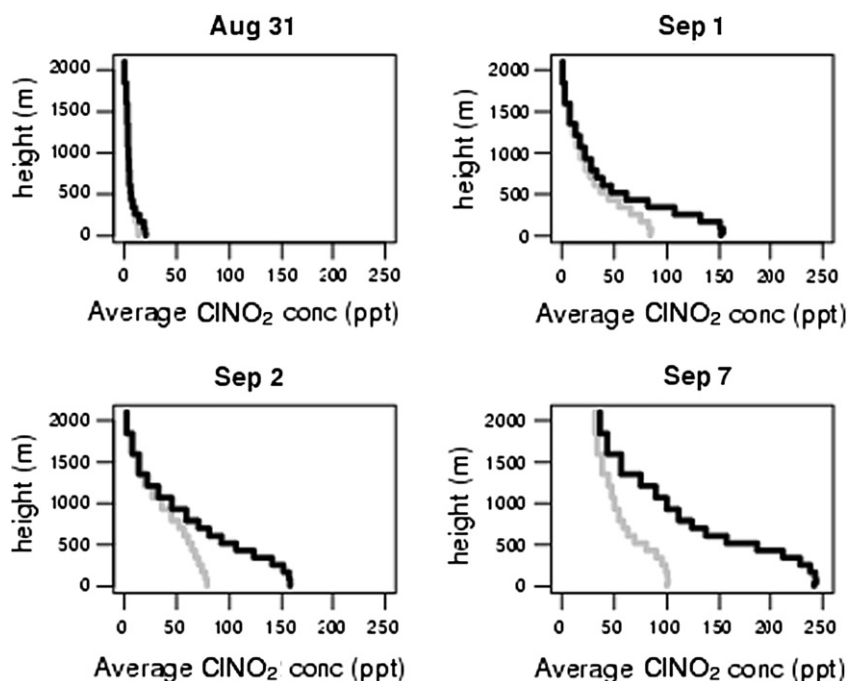


Fig. 7. Vertical profiles of average  $\text{ClNO}_2$  mixing ratios (pptv) at 1am in the 4 km domain for the base case run (gray) and the sensitivity run with excess chloride (black).

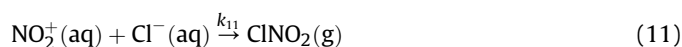
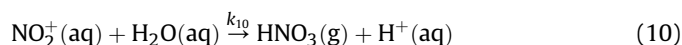
runs. Changes are calculated as the mixing ratio in the sensitivity run minus the mixing ratio in the base case run and are evaluated over the entire 4 km domain. As would be expected, there are large decreases in  $\text{ClNO}_2$  mixing ratios in the low yield run and large increases in  $\text{ClNO}_2$  mixing ratios in the high yield run.

These sensitivity runs bound the uncertainty in the magnitude of mixing ratio changes caused by the possibility of different yields.  $\text{ClNO}_2$  mixing ratios could be up to 85% lower or 70% higher if a different yield is used. These increase and decreases are upper- and lower-bounds based on observed yields in the Gulf of Mexico, but they show that the chemistry described in this work appears to be very sensitive to  $\text{ClNO}_2$  yield. It should also be noted that although the magnitude of  $\text{ClNO}_2$  mixing ratios changed with the yield, the spatial distribution of this compound remained essentially unchanged.

### 3.2.3. Explicit model representation of $\text{ClNO}_2$ yield as a function of particulate chloride concentration

All of the uncertain parameters discussed above could be more explicitly modeled by parameterizing the  $\text{ClNO}_2$  yield as a function

of particulate chloride concentration. Studies by Roberts et al. (in press) and Behnke et al. (1997) have reported  $\text{ClNO}_2$  parameterizations based on laboratory data for Reactions (10) and (11).



Both Roberts et al. (in press) and Behnke et al. (1997) fitted their data to Equation (12), reporting  $k_{10}/k_{11}$  average values of 1/450 and 1/836 respectively.

$$y = \left\{ \left( \frac{k_{10}}{k_{11}} \right) \frac{[\text{H}_2\text{O}]}{[\text{Cl}^-]} + 1 \right\}^{-1} \quad (12)$$

In Equation (12),  $y$  is  $\text{ClNO}_2$  yield,  $(k_{10}/k_{11})$  is the ratio of the rate constants for Reactions (10) and (11),  $[\text{H}_2\text{O}]$  is the molar density of water ( $\text{mol l}^{-1}$ ), and  $[\text{Cl}^-]$  is the concentration of chloride in the aqueous phase ( $\text{mol l}^{-1}$ ). Table 5 shows the particulate chloride

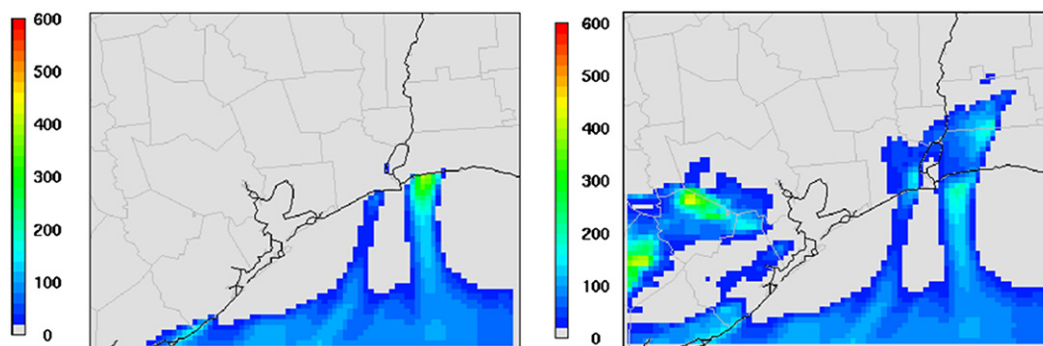


Fig. 8. Modeled  $\text{ClNO}_2$  mixing ratios (pptv) on September 4, 2006 at 8pm in the base case run (left) and in the sensitivity run which allowed inland  $\text{ClNO}_2$  formation (right).



**Table 3**Comparison of ClNO<sub>2</sub> concentration and mass in base case run and sensitivity run which allows inland ClNO<sub>2</sub> formation.

| Night of:    | Maximum ClNO <sub>2</sub> concentration in the base case run (pptv) | Maximum ClNO <sub>2</sub> concentration in sensitivity run (pptv) | ClNO <sub>2</sub> mass in the 4 km domain in base case run at 5am (metric tons) | ClNO <sub>2</sub> mass in the 4 km domain in sensitivity run at 5am (metric tons) |
|--------------|---|---|---|---|
| Aug 30–31    | 419   | 539   | 4.8   | 103.8   |
| Aug 31–Sep 1 | 1034  | 630   | 9.7   | 113.6   |
| Sep 1–2      | 1210  | 800   | 15.7  | 97.4  |
| Sep 2–3      | 362   | 241   | 16.5  | 88.6  |
| Sep 3–4      | 256   | 682   | 14.7  | 80.9  |
| Sep 4–5      | 400   | 494   | 10.7  | 97.4  |
| Sep 5–6      | 276   | 220   | 11.3  | 156.4   |
| Sep 6–7      | 1002  | 1010  | 29.6  | 125.2   |
| Sep 7–8      | 911   | 909   | 51.7  | 165.8   |
| Sep 8–9      | 882   | 2051  | 52.2  | 197.5   |

concentrations needed according to these two parameterizations to achieve different ClNO<sub>2</sub> yields.

Roberts et al. (in press) reported that during the TexAQS II/GoMACCS field campaign submicron aerosols measured on board the *Research Vessel Ronald H. Brown* had a median chloride concentration of approximately 0.04 M and a maximum chloride concentration of 1 M. Super-micron aerosols measured at the same time had a median chloride concentration of approximately 2.5 M and a maximum concentration of 10 M. This means that in the Gulf of Mexico, a ClNO<sub>2</sub> yield between 29% and 40% would be expected on submicron aerosols and a yield between 95% and 97% would be expected on super-micron aerosols.

In order to add such a parameterization to a regional photochemical model it is important that predictions of the particulate chloride concentrations be accurate. This requires an accurate chlorine inventory, accurate partitioning between gas-phase HCl and particulate-phase chloride (including acid displacement of chloride in sea salt aerosols), and accurate determination of particulate water concentrations. Figs. S7–S9 (see supplemental information) show predicted nighttime gas-phase HCl mixing ratios, [Cl<sup>−</sup>] in PM<sub>2.5</sub>, and [Cl<sup>−</sup>] in coarse PM (PM with a diameter between 2.5 and 10 μm) from a CAMx model simulation which did not include any ClNO<sub>2</sub> chemistry, but included the same emissions and meteorology of the model runs described above. The HCl and particulate chloride concentrations shown in these figures should be higher than would be predicted in a run that includes ClNO<sub>2</sub> chemistry since ClNO<sub>2</sub> formation depletes HCl/particulate chloride and cycles the chlorine into other forms. Dibb (2009) and Osthoff et al. (2008) report that HCl measurements made during TexAQS II in the Houston Ship Channel and at Moody Tower in downtown Houston rarely dropped below 0.1 ppbv. HCl mixing ratios for those areas show in Fig. S7 are generally less than this lower bound of 0.1 ppbv by a factor of two to ten. Since partitioning between HCl and particulate chloride heavily favors the gas-phase state, this

indicates that total chloride is being under-predicted in the model. This is likely due both to the large uncertainty in current anthropogenic chlorine emissions and the fact that the sea salt inventory used in this modeling included open-ocean, but not surf-zone emissions.

The [Cl<sup>−</sup>] concentrations shown in Figs. S8 and S9 can be compared to the submicron and super-micron concentrations reported by Roberts et al. (in press), although it should be noted that PM<sub>2.5</sub> concentrations will include some super-micron particles and coarse PM will not contain all super-micron particles. The comparison shows that on one night (August 30, 2006) [Cl<sup>−</sup>] concentrations in fine PM are over-predicted since the median concentration in marine regions is around 1 M and the maximum concentration is above 10 M. The plot from September 5 shows [Cl<sup>−</sup>] in the range of that reported by Roberts et al. However the plots from September 2 and September 8 show very low concentrations of [Cl<sup>−</sup>], with median values less than 0.01 M. ClNO<sub>2</sub> formation on such particles would be negligible. The [Cl<sup>−</sup>] concentration in coarse PM is greater than the range reported by Roberts et al. (in press), with median values above 10 M on several nights. The inaccuracy of model predictions for particulate chloride concentrations may be a result of under-predicted chlorine emissions, inaccurate gas/particle partitioning of HCl (specifically the movement of chloride out of coarse aerosol through reactions with HNO<sub>3</sub>), or inaccurate particulate water content predictions.

The uncertainty in the model's ability to correctly predict particulate chloride concentration in both coarse and fine PM means that explicitly representing ClNO<sub>2</sub> yield as a function of particulate chloride concentration in the current model could lead either to significant under-predictions or significant over-predictions of ClNO<sub>2</sub> formation. Over-predictions of chloride at high concentrations (above 1 M) will not have a dramatic effect on the ClNO<sub>2</sub> formation rate since the yield at 1 M is already close to 100%. For example, at 2.5 M ClNO<sub>2</sub> yield from N<sub>2</sub>O<sub>5</sub> uptake is above 95%. If the chloride concentrations were

**Table 4**Changes in ground-level ClNO<sub>2</sub> concentrations in the low and high ClNO<sub>2</sub> yield sensitivity runs in the 4 km domain. All changes in ClNO<sub>2</sub> concentrations are defined as (concentration in sensitivity run) – (concentration in base case run).

| Night of:    | ClNO <sub>2</sub> Yield = 0.18           |                                       | ClNO <sub>2</sub> Yield = 1.00           |                                       |
|--------------|--|---------------------------------------|--|---------------------------------------|
|              | Max decrease in ClNO <sub>2</sub> (pptv) | Max decrease in ClNO <sub>2</sub> (%) | Max increase in ClNO <sub>2</sub> (pptv) | Max increase in ClNO <sub>2</sub> (%) |
| Aug 30–31    | –332                                     | –86                                   | 137                                      | 68                                    |
| Aug 31–Sep 1 | –706                                     | –85                                   | 289                                      | 67                                    |
| Sep 1–2      | –896                                     | –85                                   | 373                                      | 60                                    |
| Sep 2–3      | –273                                     | –79                                   | 122                                      | 63                                    |
| Sep 3–4      | –200                                     | –78                                   | 85                                       | 45                                    |
| Sep 4–5      | –322                                     | –81                                   | 137                                      | 61                                    |
| Sep 5–6      | –194                                     | –76                                   | 72                                       | 54                                    |
| Sep 6–7      | –808                                     | –83                                   | 355                                      | 65                                    |
| Sep 7–8      | –579                                     | –80                                   | 232                                      | 57                                    |
| Sep 8–9      | –654                                     | –80                                   | 285                                      | 44                                    |

**Table 5**

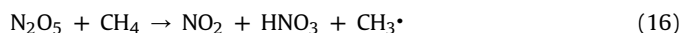
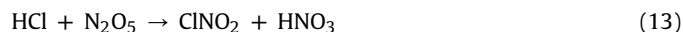
CINO<sub>2</sub> yield parameterized by [Cl<sup>−</sup>] using *k*<sub>10</sub>/*k*<sub>11</sub> values reported by Behnke et al. (1997) and Roberts et al. (in press).

| CINO <sub>2</sub> yield (%) | Required [Cl <sup>−</sup> ] (M)<br>from Roberts et al. (in press) | Required [Cl <sup>−</sup> ] (M)<br>from Behnke et al. (1997) |
|-----------------------------|---|--|
| 1                           | 0.001   | 0.001  |
| 10                          | 0.014   | 0.007  |
| 50                          | 0.123   | 0.066  |
| 75                          | 0.370   | 0.199  |
| 90                          | 1.111   | 0.598  |

over-predicted by a factor of 10 (25 M), then the yield would be above 99% (only a 4% increase). Consequently over-predictions of coarse PM chloride concentrations are not a serious concern. In contrast, either an over-prediction or an under-prediction of [Cl<sup>−</sup>] in fine PM will significantly affect CINO<sub>2</sub> formation rates. As mentioned above, at 0.05 M the expected yield is between 29% and 40%. A tenfold over-prediction in chloride concentration (0.5 M) would cause a yield of between 80% and 88%. A tenfold under-prediction in chloride concentration (0.005 M) would cause a yield of between 4% and 7%. Thus the CINO<sub>2</sub> yield is particularly sensitive to chloride concentration in the range of values found in submicron aerosols.

### 3.3. The role of CINO<sub>2</sub> in atmospheric chlorine cycling

In this model simulation, chlorine is emitted into the atmosphere in two forms: particulate chloride from sea salt emissions and Cl<sub>2</sub> from anthropogenic sources. The anthropogenic Cl<sub>2</sub> photolyzes to form chlorine radicals which proceed to participate in chemical reactions; HCl is a dominant product. This HCl can then partition into the particle-phase to form particulate chloride (the reverse phenomenon also occurs in which particulate chloride can partition to form gas-phase HCl). The particulate chloride and HCl reservoirs can be treated as one chloride reservoir since the model simulates that rapid equilibrium will be reached between gas and particle-phase chloride. Once chlorine is converted to HCl it can then react further to form CINO<sub>2</sub>, which in turn photolyzes to create chlorine radicals. As previously stated, the chlorine radicals (whether from the photolysis of Cl<sub>2</sub> or CINO<sub>2</sub>) react to form HCl and other products. Because CINO<sub>2</sub> acts both as a source and a sink for HCl, it forms a key step in chlorine cycling. Reactions (13)–(15) show an example of how this chlorine cycling can occur leading to net Reaction (16).



N<sub>2</sub>O<sub>5</sub> does not react directly with gas-phase HCl. Instead, Reaction (13) is a representation of the net process that occurs when N<sub>2</sub>O<sub>5</sub> reacts with particulate chloride and then HCl partitions into the particle form to replenish the loss of particulate chloride [essentially the same as Reaction (7)]. Reactions (13)–(15) provide a path by which chlorine may be continually cycled and reused in the atmosphere. It should also be noted that Reaction (15) is shown as one example of how Cl<sup>•</sup> can be transformed into HCl; there are a variety of other Cl<sup>•</sup> reactions in the CB IV chemical mechanism that also lead to the formation of HCl. However, without the inclusion of CINO<sub>2</sub>, there is no pathway in the chemical mechanisms used in current air quality models for non-reactive chloride (in the form of HCl or particulate chloride) to be quickly transformed back into reactive chlorine. The reaction of OH radicals with HCl to form a Cl radical and water has the potential to also cycle chlorine, but is not included in the CB IV chemical mechanism and was not considered here. In addition, it is important to note that Reaction (16) acts as a net radical source, while the OH + HCl reaction simply converts a HO<sub>x</sub> radical into a chlorine radical.

To quantify the amount of CINO<sub>2</sub> that results from the cycling described above, two more simulations were performed. These simulations modeled CINO<sub>2</sub> as a chlorine sink. Photolysis was simulated using Reaction (17) instead of Reaction (14).



One of the simulations used the N<sub>2</sub>O<sub>5</sub> chemistry from the base simulation and the other simulation used the N<sub>2</sub>O<sub>5</sub> chemistry from the inland CINO<sub>2</sub> formation sensitivity run. Comparisons of total CINO<sub>2</sub> mass present before dawn (at 5am) each morning in the runs with chlorine cycling and in the new runs which do not cycle chlorine through CINO<sub>2</sub> are shown in Table 6. Decreases in total CINO<sub>2</sub> mass from the base case heterogeneous run to the simulation using Reaction (17) range from 28 to 56%. Decreases in total CINO<sub>2</sub> mass from the original inland CINO<sub>2</sub> formation run to the simulation using Reaction (17) range from 55 to 69%. The model simulations predict that a large portion of the CINO<sub>2</sub> in Southeast Texas has cycled through CINO<sub>2</sub> on previous nights.

This cycling is important because it means that greater amount of chlorine will be in a form that is easily photolyzed into chlorine radicals which have an important impact on urban ozone formation as discussed in Simon et al. (2009) and Chang and Allen (2006a). Figs. 9 and 10 show total photolyzable chlorine mass in the simulations with and without cycling through CINO<sub>2</sub> in the base case and inland formation simulations respectively. In these simulations the

**Table 6**

Decreases in CINO<sub>2</sub> mass at 5am in the 4 km domain resulting from turning off chlorine cycling through CINO<sub>2</sub>.

| Date   | Base case run                                    |   |  | Inland Cl run                                    |   |  |
|--------|--|---|--|--|---|--|
|        | CINO <sub>2</sub> mass: Cl cycling (metric tons) | CINO <sub>2</sub> mass: no Cl cycling (metric tons) | Decrease in CINO <sub>2</sub> mass (%) | CINO <sub>2</sub> mass: Cl cycling (metric tons) | CINO <sub>2</sub> mass: no Cl cycling (metric tons) | Decrease in CINO <sub>2</sub> mass (%) |
| 31-Aug | 4.8  | 2.7   | 44                                     | 103.8  | 36.5  | 65                                     |
| 1-Sep  | 9.7  | 7.0   | 28                                     | 113.6  | 46.9  | 59                                     |
| 2-Sep  | 15.7   | 11.4  | 28                                     | 97.4   | 43.8  | 55                                     |
| 3-Sep  | 16.5   | 9.8   | 40                                     | 88.6   | 35.2  | 60                                     |
| 4-Sep  | 14.7   | 10.6  | 28                                     | 80.9   | 32.4  | 60                                     |
| 5-Sep  | 10.7   | 4.9   | 55                                     | 97.4   | 30.4  | 69                                     |
| 6-Sep  | 11.3   | 4.9   | 56                                     | 156.4  | 53.9  | 66                                     |
| 7-Sep  | 29.6   | 19.8  | 33                                     | 125.2  | 54.5  | 57                                     |
| 8-Sep  | 51.7   | 31.3  | 39                                     | 165.8  | 64.8  | 61                                     |
| 9-Sep  | 52.3   | 35.2  | 33                                     | 197.5  | 84.0  | 58                                     |

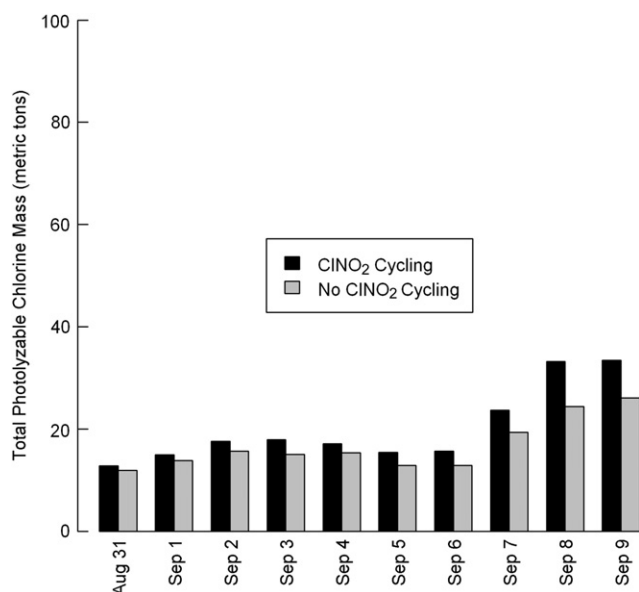


Fig. 9. Total daily photolyzable chlorine mass present ( $\text{Cl}_2$  and  $\text{ClNO}_2$ ) with and without cycling through  $\text{ClNO}_2$  for simulations that only allowed  $\text{ClNO}_2$  formation in marine grid cells.

majority of photolyzable chlorine is in the form of  $\text{Cl}_2$  and  $\text{ClNO}_2$ . Daily photolyzable chlorine mass in Figs. 9 and 10 was calculated as total 24 h emissions of  $\text{Cl}_2$  plus total  $\text{ClNO}_2$  mass present just before sunrise. These figures show that when cycling through  $\text{ClNO}_2$  is shut off, the total reactive chlorine mass in the atmosphere decreases significantly. On some days over two thirds of the reactive chlorine mass present in the atmosphere has been cycled through  $\text{ClNO}_2$ . Properly modeling this process will be important for properly simulating chlorine chemistry in regional photochemical models.

One additional factor must be considered when evaluating the impact of  $\text{ClNO}_2$  formation on chlorine cycling: deposition. HCl from the cycling pathway described above is mostly formed in the

first few hours after sunrise when  $\text{ClNO}_2$  photolyzes. For  $\text{ClNO}_2$  to play a major role in chlorine cycling, this HCl must remain in the atmosphere through the day (at least 12 h) since the  $\text{ClNO}_2$  formation process occurs predominately at night. If the deposition lifetime of HCl were short (on the order of several hours), then the majority of HCl formed through Reaction (15) and similar reactions would be lost before it could react with  $\text{N}_2\text{O}_5$  to form  $\text{ClNO}_2$ . CAMx models dry deposition based on the methods developed by Wesely (1989) which account for Henry's law, diffusion, reactivity, and surface resistance. An average deposition lifetime for the entire 4 km modeling domain (including the boundary layer and the free troposphere) was calculated as the total mass of HCl (moles) divided by the deposition rate of HCl (moles  $\text{day}^{-1}$ ). During the modeling simulation this value was 16.8 days. The lifetime with respect to deposition within the boundary layer is considerably shorter and was calculated as the average dry deposition velocity ( $\text{m s}^{-1}$ ) divided by the boundary layer height (m). The deposition lifetime for HCl during the simulation in the boundary layer was 3.1 days in marine areas and 0.74 days (17.8 h) in terrestrial areas. These deposition lifetimes for HCl are in the same range as the global deposition lifetime reported by Graedel and Keene (1995) for HCl: 1.44 days in the boundary layer and 73 days in the free troposphere. Even with the relatively short deposition lifetime of HCl in the boundary layer, reactions of particulate chloride with  $\text{N}_2\text{O}_5$  lead to significant chlorine cycling. This process appears to compete effectively with deposition as a major loss/transformation process for HCl and particulate chloride.

Previous modeling studies have looked at other chlorine cycling pathways in the atmosphere. Notably, the reaction of OH radicals with HCl to form a Cl radical and water has the potential to also cycle chlorine (Pechtl and von Glasow, 2007). However, that reaction cycles a smaller amount of Cl than the heterogeneous  $\text{N}_2\text{O}_5$  reaction pathway under the heavily polluted conditions encountered in this study. With a rate constant of  $8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , the reaction rate in heavily polluted conditions (HCl concentration of 1 ppbv and OH concentration of 0.5 pptv) is approximately 30 pptv  $\text{h}^{-1}$  during the day and much less at night when OH concentrations are small. Over the period of 12 h of sunlight, the  $\text{HCl} + \text{OH}$  reaction could create approximately 360 pptv of  $\text{Cl}^\bullet$  with no dilution, much less than  $\text{ClNO}_2$  concentrations measured by Osthoff et al. (2008). Other chlorine cycling pathways (reactions of OH,  $\text{ClONO}_2$ , and  $\text{NO}_3$  on sea salt aerosols to produce  $\text{Cl}_2$ ) have been modeled by Knipping and Dabdub (2003). They reported that the chemistry only led to maximum  $\text{Cl}_2$  concentrations of 12 pptv in the late evening and pre-dawn. The  $\text{ClNO}_2$  concentrations measured by Osthoff et al. (2008) were two orders of magnitude greater than the  $\text{Cl}_2$  concentrations from the Knipping and Dabdub modeling. Although these previous studies show that other chlorine cycling pathways may exist in the atmosphere, the ambient measurements made by Osthoff et al. (2008) are direct evidence that the  $\text{ClNO}_2$  pathway is an important chlorine cycling mechanism in a major urban area.

#### 4. Conclusions

The work reported here examined the effect of chloride limitation on  $\text{ClNO}_2$  formation using a regional photochemical model. Modeling predicted peak  $\text{ClNO}_2$  concentrations of above 1 ppbv based on parameters specific to Southeast Texas, which were in line with measurements made in this region. These concentrations may not be applicable to other regions.

This work identified key uncertainties in the modeling of heterogeneous  $\text{N}_2\text{O}_5$  chemistry including yield of  $\text{ClNO}_2$  and the availability of chloride at inland locations. Eliminating the dependence of  $\text{ClNO}_2$  formation on chloride availability caused increases in  $\text{ClNO}_2$  mixing ratios of up to a factor of 13. This suggests that chloride

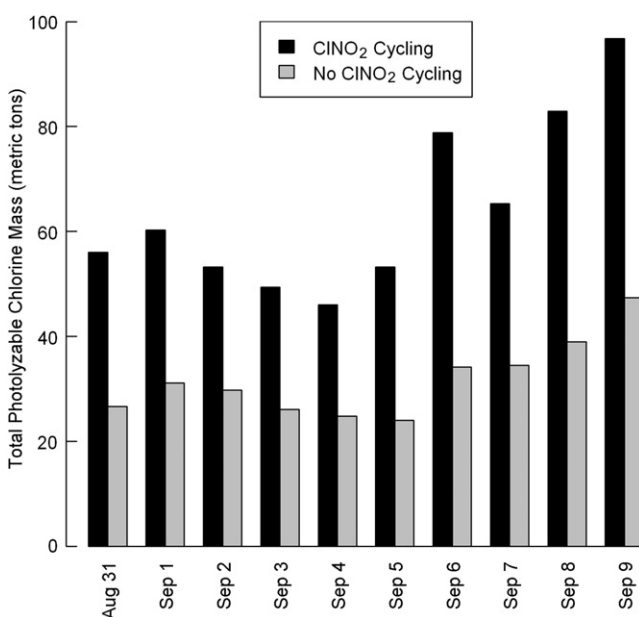


Fig. 10. Total daily photolyzable chlorine mass present ( $\text{Cl}_2$  and  $\text{ClNO}_2$ ) with and without cycling through  $\text{ClNO}_2$  for simulations that allowed  $\text{ClNO}_2$  formation both at marine and inland locations.

availability is a major limiting factor in this process at ground level. The sensitivity run which allowed ClNO<sub>2</sub> formation to occur at terrestrial locations predicted that chloride mixing ratios are high enough inland to cause significant ClNO<sub>2</sub> formation over the entire Houston area. Sensitivity runs showed that the modeled ClNO<sub>2</sub> concentration is very sensitive to yield. Although this parameter is highly uncertain, the yields used in this study are as accurate as any other in the absence of realistic model simulation for aerosol chloride molarity. Further work is suggested to increase model accuracy in predicting particulate chloride concentrations so that yield can be more accurately simulated in the future. In addition, there are two major areas for which field studies are needed to better understand the chemistry investigated in this work. First, no measurements of ClNO<sub>2</sub> have been made at inland locations. Further field work is suggested to verify the model prediction that significant ClNO<sub>2</sub> mixing ratios may occur over land. Second, more ambient measurements are needed to determine if parameterization of ClNO<sub>2</sub> yield based on laboratory data hold in the ambient atmosphere.

Finally, this work not only evaluated the effect of chloride availability on ClNO<sub>2</sub> formation, but also investigated how this formation process may affect chlorine cycling in the atmosphere. Modeling analyses suggest that chemical cycling of chlorine through HCl and ClNO<sub>2</sub> is important and that on many nights the majority of photolyzable chlorine present in the atmosphere goes through chloride/active chlorine cycling. Although modeling techniques here predict an upper-bound for the effect of ClNO<sub>2</sub> chemistry, this work shows that ClNO<sub>2</sub> plays an important role in chlorine cycling. Current photochemical air quality modeling programs do not include this cycling pathway for chlorine, so once Cl radicals react to form HCl there is no efficient pathway to convert the chloride back into reactive species. Other pathways not included in this modeling could also lead to chlorine cycling in the atmosphere (although to a lesser degree under conditions relevant to southeast Texas) and should be included in future modeling studies. The work described here has shown that in order to properly model atmospheric chlorine chemistry and its effects on urban air pollution in Southeast Texas, it will be essential to include this ClNO<sub>2</sub> formation pathway and chlorine cycling mechanism. Although this work used modeling parameterized specific to Southeast Texas, the general mechanism in which Cl cycles between HCl during the day and ClNO<sub>2</sub> at night may be more widely applicable and should be investigated more fully through modeling and measurement studies in other regions.

## Disclaimer

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## Appendix. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.atmosenv.2009.09.006.

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